

Sustainable Removal of Diazinon from Water Using a Green SiO₂/TiO₂ Emulsion Liquid Membrane

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Abstract

In this study, the removal of diazinon from synthetic aqueous solution was investigated using Hibiscus-assisted SiO₂/TiO₂-stabilized emulsion liquid membrane (ELM) system. The membrane phase consisted of xylene (as an organic diluent), Span 80 (as a surfactant), H-SiO₂/TiO₂ nanoparticles (as an interfacial stabilizer) and hydrochloric acid (as an internal stripping phase). The extraction efficiency, stripping efficiency and membrane breakage were evaluated in relation to the external phase pH, homogenizer speed, emulsification time, concentration of HCl, stirring speed, concentration of Span 80, dosage of nanoparticles and emulsification ratio. The results indicated that diazinon removal was governed by the interfacial mass-transfer/emulsion-stability ratio. The optimum values and ranges of operating conditions for the tested systems were pH 7, homogenizer speed, 5800 rpm, emulsification time, 6 min, HCl concentration, 0.15 M, stirring speed, 250 rpm, Span 80 concentration, 2% v/v, and H-SiO₂/TiO₂ dosage, 0.4 mg. The ratio of emulsion to external phase (20:100) yielded the highest extraction efficiency of 96.35% and the 20:75 ratio exhibited higher stripping efficiency and lesser membrane breakage rates. The recyclability tests showed that the membrane maintained good performance up to three reuses, with a decrease in performance being observed with the fourth and fifth reuses. These results indicate that the H-SiO₂/TiO₂ assisted ELM system can be used as an effective method to remove diazinon from aqueous solution; however, more testing needs to be done with actual wastewater matrices to demonstrate this.

Keywords:

Diazinon; Emulsion liquid membrane; H-SiO₂/TiO₂ nanoparticles; Span 80; Pesticide removal; Membrane stability; Aqueous solution treatment

1. Introduction:

Since the middle of the last century, pesticides have been vital to modern agriculture, especially for crop protection and enhancing agricultural production. However, they have been overused and, in some cases, left uncontrolled, causing serious environmental issues, particularly the pollution of surface and groundwater. Organophosphorus pesticides are one of the various classes of pesticides, introduced in the 1960s as alternatives to persistent organochlorines (OC) such as DDT and aldrin. Despite being less persistent than OCPs, OPPs still pose persistent environmental and public health risks because they are still used and may be released into aquatic environments (Baharum et al., 2020; Mansouriieh et al., 2016).

Diazinon (O,O-diethyl O-[4-methyl-6-(propan-2-yl) pyrimidin-2-yl] phosphorothioate) ranks among the organophosphorus pesticides with the widest use, finding application in both farming operations and domestic environments. The pesticidal activity is primarily attributed to its ability to inhibit cholinesterase and impair normal nerve function in target organisms. However, this does not limit the risk of diazinon; it can be harmful to other organisms in the environment as well, and can have potential health effects in contaminated water. Hence, the removal of diazinon from water has become an important concern in environmental remediation and water treatment (Abkenar et al., 2023).

Physicochemical properties of diazinon are essential for selecting an appropriate removal method. Diazinon is low soluble in water, and its octanol–water partition coefficient is relatively high, suggesting that it is

mainly hydrophobic. This behavior means diazinon is not always fully aqueously bound, leading to some affinity for organic phases. The relevance of extraction-based systems for extracting this compound is underscored by this property. Concurrently, it is moderately soluble and present at low concentrations in contaminated waters, which may compromise the efficiency of some traditional treatment methods that require high selectivity and rapid mass transfer (Ahmadi et al., 2020).

Researchers have explored numerous strategies for eliminating pesticide residues from aqueous media, spanning activated carbon adsorption, biological treatment, Fenton oxidation, membrane filtration, reverse osmosis, and photocatalysis based on TiO_2 . These techniques are effective under certain operating conditions but can present disadvantages, including high operating costs, long treatment times, low degradation rates, generation of secondary waste, or decreased selectivity in complex water matrices. Alternative separation processes have been developed to address the limitations of these methods, such as those that can effectively remove hydrophobic organic contaminants under relatively simple operating conditions (Costa et al., 2018; Dâas & Hamdaoui, 2014).

Of these strategies, emulsion liquid membrane (ELM) technology has drawn growing interest, owing to its practicality and efficiency for treating water contaminated with organic pollutants. In a conventional W/O/W (water-in-oil-in-water) configuration, the pollutant of interest sits within the outer aqueous phase, the organic membrane serves as a selective barrier governing transport, while the inner aqueous phase gathers and concentrates the solute once extracted. What distinguishes this configuration is its ability to combine extraction and stripping into one simultaneous step, eliminating the need for separate stages. Owing to diazinon's hydrophobic character, the organic membrane phase is naturally inclined to extract it from the feed solution and convey it toward the stripping phase. Equally critical is the internal stripping phase, which maintains the concentration gradient responsible for continuously pulling diazinon from the feed side into the recovery side (Al-Damluji & Mohammed, 2023; Rosly et al., 2020).

Although emulsion liquid membrane technology is useful, its application is sometimes limited by emulsion instability. Breakage, swelling of the membrane, and coalescence of droplets can reduce the actual interfacial area and lead to deterioration of the membrane, with consequent declines in both extraction efficiency and the overall reliability of the process. Such effects reduce extraction efficiency and reliability. Protective agents such as Span 80 are used as stabilizers in water-in-oil emulsions because they reduce interfacial tension and form a protective film around the water droplets. But too much surfactant can increase solution viscosity, reduce mass transfer, and make phase separation more difficult. Thus, achieving these conditions while maintaining emulsion stability remains a main challenge for ELM applications (Kusumastuti et al., 2020; Zeresghi et al., 2021).

Although ELM systems have many benefits for pesticide elimination in practice, emulsion instability, interaction between components, and a lack of knowledge regarding the significance of stabilizing agents have hindered their use. Hence, the current study focuses on extraction of diazinon, stability of membrane and reusability of membranes using the two processes of combined Span 80 and $\text{SiO}_2/\text{TiO}_2$ nanoparticles, with an awareness of the necessity for testing in actual wastewater matrices in the future.

Here, $\text{SiO}_2/\text{TiO}_2$ nanoparticles synthesized via hibiscus plant extract were integrated into an ELM system designed to eliminate diazinon from water. The plant-assisted synthesis route was chosen because it reduces the use of harsh preparation conditions and makes the nanoparticle synthesis route considerably more eco-friendly. This work examined the influence of multiple operating parameters on overall performance, namely feed pH, homogenizer speed, emulsification duration, internal HCl concentration, stirring speed, Span 80 content, nanoparticle loading, and the volumetric ratio of emulsion to external phase. The primary goal is to predict the conditions that maximize diazinon extraction and stripping efficiencies while

minimizing membrane damage and breakage, and to rationalize the observed behavior in terms of physicochemical interactions among diazinon, the membrane phases, and the SiO₂/TiO₂ nanoparticle stabilizers.

2. Materials and methods

All chemicals used in this study were of analytical grade. Diazinon (98% purity) was purchased from a certified supplier in the agricultural sector. Tetraethyl orthosilicate (TEOS), titanium isopropoxide, Span 80, xylene, hydrochloric acid (HCl, 37%), nitric acid, and ethanol were obtained from Sigma-Aldrich. The dried calyces of *Hibiscus sabdariffa* were obtained locally and used as the extract. All experimental procedures were carried out using distilled water.

2.1. Equipment

The concentration of diazinon in aqueous samples was measured by the UV–Vis spectrophotometer (Thermo Scientific, USA) at 248 nm. An SR30 (Korea) digital homogenizer was used to emulsify. During the extraction step the external phase was stirred at controlled rotational speeds by a digital overhead stirrer (Heidolph RZR 2021, Germany; operating range from 0 to 2200 rpm; impeller diameter of 5 cm).

The morphology of the emulsion was observed by an optical microscope (Olympus BX51, Japan, 1 μ m @ 1500 $\times$). For the extraction phase, separation was facilitated using a centrifuge (Hettich, Germany). A heated magnetic stirrer plate (IKA, Germany) was also used to facilitate further mixing during the synthesis of the nanoparticles. Adjustments of the pH of aqueous solution were made with 1 N HCl or 1 N NaOH.

2.2. A stock solution of diazinon and calibration.

A stock solution of diazinon was prepared by accurately weighing diazinon crystals, dissolving them in a minimal volume of ethanol, and subsequently diluting to the desired final volume with distilled water. Working solutions of diazinon were obtained by serial dilution of the stock solution to yield concentrations of 5, 10, 25, 50, 75, and 100 mg/L.

The concentration of diazinon was determined by UV-Vis spectrophotometry at a wavelength of 248 nm. Absorbance measurements were recorded against distilled water as a blank reference, and a calibration curve was constructed by plotting absorbance as a function of diazinon concentration. The calibration equation was written as a function of the changes in the variable, R, as follows:

$$A = mC + b$$

The absorbance (A) is related to the concentration of diazinon (C) in mg/L by a linear equation: $A = mC + b$, where m is the slope and b is the intercept.

The calibration equation that was obtained was:

$$A = 0.0142C + 0.0031 \quad (R^2=0.983) \dots\dots\dots (1)$$

Both the limit of detection and the limit of quantification were determined using:

$$LOD = 3\sigma/m$$

$$LOQ = 10\sigma/m$$

The standard deviation of the blank response, σ , and the slope of the calibration curve, m. The calculated LOD and LOQ were 0.08 mg/L and 0.27 mg/L, respectively.

When necessary, all samples were diluted to fall within the linear range of the calibration curve for measurement. Blank samples were measured and were treated with the same components present in the matrix as a reference, except for diazinon, to eliminate potential spectral interference from span 80, xylene, HCl and nanoparticles, respectively. Furthermore, all samples were filtered through a syringe filter (0.22 μ m) before UV–Vis analysis.

2.3. Preparation of Hibiscus-assisted SiO₂/TiO₂ nanoparticles

2.3.1. Preparation of Hibiscus extract

Dried calyces of *Hibiscus sabdariffa* were milled into a fine powder, after which 10 g of this powder was combined with 100 mL of distilled water and maintained at 80°C for 30 min under continuous stirring. Once heating was complete, the mixture was passed through Whatman No. 1 filter paper to separate the solids, and the resulting aqueous extract was kept refrigerated at 4°C until it was required for use.

2.3.2. Nanoparticle synthesis

Hibiscus-assisted SiO₂/TiO₂ nanoparticles were synthesized via a modified sol–gel/hydrothermal procedure based on the methodology reported by Yang et al. (2018). Briefly, tetraethyl orthosilicate (TEOS; 5 mL) and titanium isopropoxide (15 mL) were sequentially introduced to an ethanol solution containing 12% v/v Hibiscus extract under continuous magnetic stirring. Nitric acid (0.1 mL) and deionized water (4 mL) were subsequently added dropwise to promote controlled hydrolysis and condensation of the precursor materials. The resulting sol was maintained at room temperature with continuous stirring for 2 h until gelation was complete. The gel was then aged for 24 h at room temperature.

Once the aging period was complete, the gel was placed into a stainless steel autoclave and underwent hydrothermal treatment at 245°C for 2 h in a nitrogen atmosphere. Following cooling to room temperature, the solid product was purified through a sequential washing procedure, comprising three rinses with deionized water and a final rinse with ethanol, in order to eliminate any remaining reagents and unreacted precursors. The cleaned material was then dried at 80°C for 12 h, carefully ground into a fine powder, and placed in a sealed container until it was ready for characterization and subsequent use in the emulsion liquid membrane system.

2.4. Characterization of SiO₂/TiO₂ Nanoparticles Enhanced by Hibiscus

Hibiscus-assisted SiO₂/TiO₂ nanoparticles were characterized before and after diazinon extraction to evaluate the morphology, surface functional groups, and crystalline structure.

2.4.1. Scanning electron microscopy

Scanning electron microscopy was used to examine surface morphology, particle shape, and degree of agglomeration of the synthesized H-SiO₂/TiO₂ nanocomposite. The particles were mainly spherical, with diameters between 48 and 66 nm, and exhibited irregular aggregation, a rough, porous surface with visible grooves and channels (Fig. 1). This surface structure offers a large number of available sites and is consistent with the measured BET surface area of 450 m²/g and total pore volume of 0.2694 cm³/g.

SEM images (Figs. 1.a & 1. b) were taken before and after diazinon extraction to assess possible surface changes. After extraction, the particles exhibited a smoother surface texture and some aggregate fusion, which could be attributed to diazinon interacting with the nanoparticles' surface, as observed in similar oxide-based systems (Hlophe & Dlamini, 2021).

Fig. 1.a: SEM photos of H-TiO₂/SiO₂
Before treatment at 200nm magnification

Fig. 1.b: SEM photos of H-TiO₂/SiO₂ after
treatment at 200nm magnification

2.4.2. FTIR Spectroscopy

FTIR analysis was carried out to identify the main functional groups present on the surface of H-SiO₂/TiO₂ before and after diazinon extraction. The spectra were recorded between 4000 and 400 cm⁻¹. In curve S1 in Fig. 2, the surface hydroxyl group and the water molecule on the pristine nanocomposite showed a wide absorption band that is generally assigned to the O–H stretching vibrations in the range of 3300–3500 cm⁻¹ (Ma et al., 2015). The band at 3443.28 cm⁻¹ was identified as the N–H stretching band in the organic residues of hibiscus (Verma et al., 2022). The formation of the composite oxide structure was confirmed by the peaks at 1633.41 cm⁻¹, attributed to Ti–O stretching, and at 667.25 cm⁻¹, attributed to Si–O–Si bending (Mohtashamian et al., 2013). The band at 1052.94 cm⁻¹ was assigned to C–O vibrations of the remaining organic components of the Hibiscus extract.

Following the diazinon extraction (curve S2 in Fig. 2), single-peak shifts and changes in relative intensities were observed, with weak bands noted. The changes suggest a surface interaction between diazinon and the nanocomposite. The main structural bands of the H-SiO₂/TiO₂ framework, however, did not show surface interactions with diazinon or significant changes following the extraction process, indicating that there was no severe structural damage in the nanocomposite.

Fig. 2: Transformation of FTIR Spectrum of H-TiO₂/SiO₂ Nanoparticles Following Treatment

2.4.3. X-Ray Diffraction analysis:

A crystalline phase composition for the synthesized H-SiO₂/TiO₂ nanocomposite was determined using X-ray diffraction. Based on JCPDS card no. 21-1272, the diffractogram (Fig. 3) showed characteristic diffraction peaks at 11°, 15°, 24°, 24.6°, and 25°, consistent with tetragonal anatase phases of TiO₂ (Hussain et al., 2024). It was concluded that an amorphous SiO₂ phase is present in the prepared composite between 10° and 25° 2θ, identified as a broad diffuse band.

Fig. 3: XRD patterns of H-TiO₂ /SiO₂ nanocomposites.

The mean crystallite size was estimated using the Debye–Scherrer equation from the most broadened anatase peak.

$$D = K \cdot \lambda / \beta \cdot \cos\theta \dots\dots\dots (1)$$

These are known as the crystallite size, shape factor (K), X-ray wavelength (λ), and full width at half maximum of the diffraction peak (β) and the Bragg angle (θ). The calculated crystallite size is around 17.5 nm, which supports that the material is a nanograin material.

2.5. Emulsion Liquid Membrane Preparation

The ELM system was composed of three stages: an organic membrane phase, an internal aqueous stripping phase, and an external aqueous feed phase with the diazinon (Mohammed et al., 2020).

Membrane phase: The organic membrane phase, with a total volume of 25 mL, was formulated by combining Span 80 (at the specified concentration, % v/v) with a defined quantity of SiO₂/TiO₂

nanoparticles. This mixture was agitated for 10 minutes on a magnetic stirrer to achieve uniform and stable dispersion of the nanoparticles throughout the organic phase.

Internal stripping phase: An HCl solution of the required molar concentration was prepared using water to serve as the internal stripping phase. A 5 mL portion of this solution was added dropwise into the membrane phase while the system underwent continuous homogenization in the SR30 digital homogenizer for 15 minutes at a controlled speed. This procedure yielded a primary emulsion characterized by finely dispersed internal water droplets suspended within the organic membrane phase, referred to as a water-in-oil (W/O) primary emulsion (Hussein & Ahmed, 2025).

During the extraction stage, the W/O emulsion was dispersed into 50–100 mL of an external aqueous feed phase that had been prepared with an initial diazinon concentration of 100 mg/L. Mild agitation was applied using an overhead stirrer operating at a controlled speed, which promoted the transfer of diazinon from the external phase, across the organic membrane, and ultimately into the internal stripping phase. At predetermined time intervals, aliquots were collected from the external phase, passed through a 0.22 μm syringe filter, and subsequently quantified using UV-Vis spectrophotometry.

Demulsification: After the extraction process, W/O emulsion was demulsified by gravity settling and then by centrifugation. The recovered emulsion was then subjected to demulsification to separate the internal stripping phase from the organic membrane phase. The diazinon striped concentration was then quantified. The entire ELM procedure is illustrated on Fig. 4.

Fig.4: diagram of the emulsion procedure

2.5. Analysis and Calculations:

The extraction and stripping efficiencies were calculated as follows. The concentration of diazinon in the external aqueous phase was determined at each sampling point by UV-Vis spectrophotometry. The extraction efficiency (E%) was calculated according to:

$$E \% = \frac{C_{eo} - C_{et}}{C_{eo}} * 100 \quad \dots\dots\dots (2)$$

The external phase concentration of diazinon at time t is represented by C_{et} and the initial concentration of diazinon in the external phase is represented by C_{eo} .

The stripping efficiency (%S) was determined by:

$$S \% = \frac{C_{if}}{C_{eo} - C_{ef}} * 100 \quad \dots\dots\dots (3)$$

The final concentrations of diazinon in the external phase (C_{ef}) and the internal phase (C_{if}) are used.

The amount of change in the external phase pH during extraction was used to calculate the emulsion breakage percentage (% ξ) according to Mohammed et al., (2020) mass balance equation:

$$\xi \% = \frac{V_i}{V_{i0}} * 100 \quad \dots\dots\dots (4)$$

with V_i / V_{i0} determined using the mass balance relation:

$$V_i = V_{e0} \frac{10^{-pH_0} - 10^{-pH}}{10^{-pH} - C_{H^+}^{int}} \quad \dots\dots\dots (5)$$

In this expression, pH_0 denotes the initial pH of the external phase, V_{e0} represents the initial volume of the external phase, $C(H^+)_{int}$ corresponds to the initial hydrogen ion concentration within the stripping phase, and pH refers to the pH of the external phase measured after a defined time interval.

2.6 Experimental design

A one-factor-at-a-time (OFAT) optimization approach was adopted to systematically evaluate how the key operating parameters influenced three critical performance indicators: diazinon extraction efficiency, stripping efficiency, and membrane breakage. Under this strategy, a single parameter was deliberately altered in each set of experiments, while all remaining variables were kept fixed at their established baseline levels, thereby allowing the individual contribution of each factor to be isolated and clearly assessed.

The parameters subjected to investigation encompassed the external phase pH, homogenizer speed, emulsification time, Span 80 concentration, HCl concentration, H-SiO₂/TiO₂ nanoparticle dosage, stirring speed, and the emulsion-to-external-phase ratio. To ensure the reliability and reproducibility of the findings, every experiment was conducted in triplicate, and the corresponding results are reported as the mean $\pm$ standard deviation. A detailed summary of the experimental conditions applied throughout these tests is provided in Table 1.

Table 1. Experimental parameter ranges investigated in this study.

2.7 Quality Control and Method Limitations

A blank reagent was prepared and measured under the same spectrophotometric conditions to compensate for the absorbance interference at 248 nm caused by the components of the experimental matrix such as xylene, Span 80, HCl and H-SiO₂/TiO₂ nanoparticles. To minimize the turbidity interference, samples were filtered through a syringe filter with 0.22 μ m before analysis by UV–Vis. Each extraction was carried out three times, and the results are given as mean $\pm$ SD.

It is important to note that none of the following control experiments were part of the present experimental design: diazinon solution without ELM treatment, ELM without H-SiO₂/TiO₂ nanoparticles, ELM without Span 80, and direct adsorption by dispersed H-SiO₂/TiO₂ nanoparticles. The following controls are suggested for future studies to determine the effect of each of these factors separately: volatilization, vessel-wall adsorption, nanoparticle adsorption, surfactant stabilization, and nanoparticle-assisted interfacial stabilization.

2.8 Statistical Analysis

The experiments were repeated three times, and the results were reported as mean $\pm$ SD. The error bars given in the Figures are based on the standard deviation of three independent measurements.

3. Results and discussion:

3.1. Effect of External Phase pH

The pH of the external phase had a small but significant effect on the extraction of diazinon. A decrease in C/C_0 with time was observed for all the pH values (3, 7, and 10) as shown in Fig.5, suggesting that the progressive transfer of diazinon from the external aqueous phase to the emulsion liquid membrane system (ELMS) continued. The minimum residual concentration was measured at pH 7, but the differences between the various pH levels tested were not significant. Therefore, pH should not be regarded as the most important factor in determining diazinon extraction. This handling is similar to that of diazinon due to its physicochemical properties. The water solubility of diazinon is moderate to low, reported as 40-60 mg/L, and the log K_{ow} is around 3.3, indicating a tendency to partition towards the organic phases rather than remain fully in the aqueous phase. In the current ELM system, therefore, the affinity of diazinon for the organic membrane phase plays a predominant role in the transfer of the compound, while pH has a dominant effect on emulsion stability and interfacial behavior. The slightly weaker extraction profile at acidic pH can be explained by membrane instability and/or an osmotic difference between the external aqueous phase and the internal HCl phase. The extraction profile was not ameliorated under alkaline conditions, either, indicating partial destabilization of the surfactant-supported oil–water interface. For this reason, pH 7 was chosen for further studies, as the extraction profile was found to be the most stable among the values tested. This result suggests that the optimum is not due to any significant pH-selective extraction but to stability.

Fig.5: Normalized diazinon concentration (C/C_0) during extraction with H-SiO₂/TiO₂-assisted emulsion liquid membrane system as the external phase pH was changed. Error bars are shown as standard deviation of the triplicates (n = 3).

3.2. Effect of Homogenizer Speed

Homogenizer speed had an influence on the performance of the ELM system because the quality of the dispersion of the primary water-in-oil emulsion and expands the surface area accessible for diazinon transport. When speed was raised from 3000 to 5800 rpm, extraction efficiency climbed from roughly 81% to 92%, while stripping efficiency increased from about 79% to 88% (Fig. 6.a). This improvement suggests that not enough interfacial contact was achieved between the emulsion and the oil for efficient extraction and stripping when the emulsion was prepared at 3000 rpm. Improved dispersion achieved at higher rotational speeds expanded the interfacial area and eased the transfer of solute through the membrane (Sabry et al., 2007; Jusoh et al., 2016).

Taken together, 5800 rpm produced the most favorable outcomes overall. This does not necessarily indicate that this speed gave the most stability for the membrane. Membrane breakage was also observed to increase at 5800 rpm as compared to 3000 rpm. Thus, the result is a balance of improved interfacial area and transfer of diazinon which outweighed increased partial membrane leakage. Hence, 5800 rpm is an optimum point for extracting-stripper and not a minimum-breakage point.

The extraction and stripping efficiencies decreased significantly if the homogenizer speed was increased beyond 12700 rpm. Even if the breakage percentage measured is not the highest, the excess shear can disrupt the surfactant/nanoparticle supported interfacial layer, and lower the functional stability of the emulsion. This validates that the breakage of the membrane is not enough to assess the performances of ELM. For efficient extraction, the droplet structure, interfacial area and interfacial stability should be appropriate to allow the transport of solutes to the external phase when it comes in contact with the droplets (Kusumastuti et al., 2020; Othman et al., 2017; Zereszki et al., 2021).

The optical micrographs in Fig. 6.b tend to substantiate this interpretation. They indicate that the droplet size and shape were significantly altered by the homogenizer size. The emulsion that was prepared at 5800 rpm seemed to give better droplet dispersion for the transport of diazinon, while the emulsion prepared at 12700 rpm did not directly reflect the increase in shear. The micrographs are qualitative and the size of the droplets cannot be quantitatively compared based on the scale bars, as these have not been the same size throughout the images. Rather, they agree with the conclusion reached in Fig. 6a, that the maximum mass transfer obtained at the lowest rotational speed that is still acceptable for membrane stability was 5800 rpm.

Fig. 6.a. Effect of homogenizer speed on diazinon extraction efficiency, stripping efficiency, and membrane breakage by H-SiO₂/TiO₂-assisted emulsion liquid membrane system.

Fig. 6.b. Optical microscopy images of the W/O emulsion droplets from different homogenizer speeds.

3.3. Effect of Emulsification Time

Emulsification time was related to the quality of the water-in-oil emulsion and directly impacted the transport of diazinon. The higher emulsification time (from 2 min to 6 min) boosted the extraction efficiency from 68.57% to 93.25% and the stripping efficiency from 63.54% to 86.24% (see Fig. 7). Concurrently, the percentage of membrane breaking dropped from 2.8% to 1.2%. This shows that the emulsion prepared at

short emulsification times was not sufficiently developed, as it was found that there was more extraction but less stripping and breakage.

The presence of the internal HCl phase was most likely dispersed as larger or less uniform drops in the organic membrane phase at 2 and 4 min. This type of structure provides less interfacial area within the membrane for stripping and less efficiency for transport of diazinon. Lengthening the emulsification step to 6 min yielded a more uniform emulsion, which enhanced both extraction and stripping performance without compromising membrane integrity. In ELM systems, droplet dispersion and mass transfer efficiency can be improved with proper emulsification while maintaining the emulsion structure, as long as it is stable (Chaouchi & Hamdaoui, 2014).

After 6 min, no improvement was seen. Extract efficiency decreased to 80.25% and 74.24% at 8 min and 10 min, respectively, and stripping efficiency also dropped with an increase in the number of membrane breaks. Most likely this decrease is due to over-emulsification. After a desirable internal dispersion of droplets is reached, additional shear is not always beneficial in generating useful interfacial area. Rather, it could impair the interfacial film on Span 80/H-SiO₂/TiO₂ and/or cause swelling and/or partial coalescence. When mechanical stress is beyond the ELM stability limit, these instability mechanisms can cause ELM performance degradation (Kusumastuti et al., 2020; Zeresghi et al., 2021).

Accordingly, 6 min was identified as the most favorable emulsification duration. The optimum extraction efficiency, the maximum stripping efficiency and the minimum membrane breakage were obtained with the condition at 6 min. of emulsification. As a result, emulsification time should be optimized rather than simply prolonged.

Fig. 7. Effect of emulsification duration on diazinon extraction and recovery within the H-SiO₂/TiO₂-assisted emulsion liquid membrane system, derived from triplicate measurements (n = 3).

3.4. Effect of HCl Concentration

The concentration of hydrochloric acid in the internal stripping phase played a decisive role in governing both the transport of diazinon across the membrane and the overall stability of the membrane itself. As illustrated in Fig. 8, increasing the HCl concentration from 0.05 to 0.15 M produced a marked improvement in performance: the extraction efficiency rose from 80.54% to 93.25%, while the stripping efficiency climbed from 75.23% to 86.57%. In parallel with these gains, the extent of membrane breakage declined considerably, decreasing from 2.8% to 1.2%. These observations suggest that, at the lower concentration of 0.05 M HCl, the driving force for mass transfer was insufficient, as the limited acid availability failed to establish an adequate concentration gradient across the organic membrane to promote effective diazinon transport.

The movement of diazinon from the xylene-based membrane phase into the aqueous stripping phase was dictated by the concentration gradient and the chemical potential difference present across the liquid-liquid interface, an effect most pronounced at the higher HCl level of 0.15 M. This resulted in lower diazinon levels in the membrane and continuous removal from the aqueous phase outside the membrane. The internal stripping phase is crucial for ELM systems because it ensures the chemical potential gradient that is

necessary for coupled extraction and stripping, thereby enhancing the efficiency of removal and recovery when the gradient is high enough (Al-Damluji & Mohammed, 2023; Othman et al., 2017).

However, elevating HCl to 0.5 M lowered extraction efficiency to 74.65% and stripping efficiency to 70.14%, while membrane breakage climbed to 3.2%. This drop reflects that too much internal-phase acidity did not increase stripping but rather destabilized the emulsion. The above effect can be enhanced by a high internal phase concentration, which increases the osmotic imbalance between the internal stripping phase and the external aqueous phase, causes internal droplets to swell, and can reduce the strength of the film of surfactant/nanoparticles at the interface. These effects cause leakage and diminish the area of the membrane for diazinon transport. Swelling, leakage, and droplet coalescence remain intrinsic constraints of ELM systems, although incorporating H-SiO₂/TiO₂ nanoparticles helps reinforce the membrane (Zereshki et al., 2021).

On this basis, 0.15 M HCl offered the most favorable trade-off between transport efficiency and membrane stability, leading to its selection as the optimal stripping concentration. It gave the maximum extraction efficiency, maximum stripping efficiency and minimum of membrane breakage at all concentrations tested. The findings showed that a higher concentration of stripping agents up to the point of maintaining the structural stability of the emulsion was advantageous.

Fig. 8. Influence of HCl concentration on diazinon extraction, stripping efficiency, and membrane breakage within the H-SiO₂/TiO₂-assisted emulsion liquid membrane system.

3.5. Influence of Stirring Rate

The stirring rate determined the rate of contact between the emulsion drops and the external diazinon solution. As shown in the Fig. 9, the stirring rate 250 rpm resulted in the higher extraction efficiency of 93.25% and 84.35% stripping efficiency compared to the rate of 150 rpm. The percentage of membrane breakage also went down from 2.7% to 1.1%. Mixing at 150 rpm proved too mild, leaving emulsion globules with limited contact with the diazinon-bearing feed and creating resistance to mass transfer. By contrast, at 250 rpm droplets spread more evenly throughout the external phase, establishing conditions more conducive to solute transport.

Hence, the optimum operating condition for the system was found at 250 rpm. The agitation intensity was sufficient to enhance the transfer of diazinon from the external aqueous phase to the organic membrane, and subsequently to the internal stripping phase. Meanwhile, the emulsion was also sufficiently stable, as indicated by the lowest breakage value. Efficient extraction in ELM systems requires achieving a balance between external mixing and maintaining the integrity of the membrane, without compromising either process (Rosly et al., 2020).

At 350 rpm, intensified mechanical shear started to distort the emulsion globules and erode their protective interfacial layer, triggering leakage and pulling both extraction and stripping efficiency down to 86.57% and 78.54%, respectively. However, the percentage of membrane breakage rose to 3.6%. This drop indicates that the emulsion was not improved by over-agitation, but by disruption of the emulsion. Shear in the extraction step may cause a distortion of the emulsion drops, leakage of the inner phase, and thinning of the layer of surfactant and nanoparticles. This instability, such as swelling, leakage, and coalescence is known as a weakness of ELM operation (Kusumastuti et al., 2020).

Thus, 250 rpm was chosen as the best stirring rate. It offered the greatest extraction and stripping efficiencies and least membrane breakage. It is found that the stirring rate should be enough to ensure that no external mass transfer resistance is present, but not so high as to cause mechanical damage to the emulsion.

Fig. 9. Diazinon extraction efficiency, stripping efficiency, and membrane breakage as a function of stirring speed using the H-SiO₂/TiO₂-assisted emulsion liquid membrane system. Three triplicate measurements (n = 3) were used to calculate the standard deviation.

3.6. Effect of Span 80 Concentration and H-SiO₂/TiO₂ Nanoparticle Dosage

ELM system performance was a function of both the concentration of Span 80 and the dosage of H-SiO₂/TiO₂ nanoparticles, but not in a linear fashion. As seen in Fig. 10.a, higher extraction efficiency of diazinon was obtained with an increase in the concentration of Span 80, from 1% v/v to 2% v/v (from 70.47% to 80.23%) and efficiency of stripping also improved from 65.23% to 73.54% at 2% v/v of Span 80. In the same range, the breakage of the membrane reduced from 2.7% to 0.8%. This means that 1% Span 80 was not enough to completely stabilize the water in oil interface, and thus the emulsion is more prone to leakage and coalescence.

The recommended concentration for Span 80 was 2% v/v because it gave the best extraction efficiency and membrane stability. Concentration of the surfactant was adequate to decrease interfacial tension and stabilize the inner droplets without the development of an excessive resistance to the transport of diazinon through the membrane phase. In ELM systems, the impact of the surfactant concentration on stability and the mass-transfer resistance have been reported (Aleid et al., 2025).

No improvement was observed on extraction performance to Span 80 even though the concentration was increased to 3% v/v. Efficiency declined a little to 78.25% and membrane breakage rose to 1.5%. The above indicates that further useful surfactant concentration at the organic phase did not occur at 2% v/v, which may be due to the increase in membrane viscosity and the decrease in the solute diffusion across the organic phase. From Fig. 10.a, it was found that 2% v/v Span 80 was the best surfactant concentration.

The dosage effect of H-SiO₂/TiO₂ nanoparticles was more significant. Comparing the two figures, Fig. 10.a and Fig. 10.b, it can be observed that higher dosage of nanoparticles from 0.2 mg to 0.4 mg resulted in the improvement of extraction efficiency (76.85%-93.25%) and stripping efficiency (70.14%-84.67%) with a decrease in membrane breakage (0.156%-0.042%). This improvement revealed that the nanoparticles enhanced the oil–water interface and lessened the instability of the droplets. The solid particles in Pickering type systems form an oil/water interface barrier to prevent droplet coalescence (Xiao et al., 2025). Another possible contribution from the H-SiO₂/TiO₂ surface would be the surface hydroxyl groups and high surface area, which may help organize and stabilize the membrane interface (Yang et al., 2024) .

The extraction efficiency decreased to 86.34%, and stripping efficiency was also decreased to 78.64% with further increase in the dosage of the nanoparticles from 0.6mg and membrane

breakage increased slightly to 0.054%. This signifies that further increase of loading the nanoparticles doesn't improve the ELM performance further. After a certain thickness of the interface is covered, the additional particles may cause aggregation or form a denser interfacial film, which will lead to higher mass transferring resistance across the membrane. There are similar trade-offs for ELM systems, where too much stabilizing material can make the setup appear more robust, but could also decrease transport efficiency (Shokri et al., 2020). Thus, the best operating conditions under the experimental conditions were 2% v/v Span 80 and 0.4 mg H-SiO₂/TiO₂. These conditions provided the highest extraction efficiency, highest stripping efficiency and lowest membrane breakage. The results indicate that Span 80 and H-SiO₂/TiO₂ were synergistic; Span 80 created the main surfactant film and the nanoparticles strengthened the interface to prevent coalescence.

Fig. 10. Effect of (a) Span 80 concentration and (b) H-SiO₂/TiO₂ nanoparticle dosage on extraction efficiency, stripping efficiency, and membrane breakage.

3.7. Effect of Emulsion-to-External Phase Ratio

The extent of diazinon removal was clearly shaped by the volumetric ratio between the emulsion and the feed solution. As the ratio was raised from 20:50 to 20:100, extraction efficiency climbed steadily, reaching a maximum of 96.35% (Fig. 11). Such gains can be attributed to the 20:100 emulsion-to-external phase ratio, which supplied adequate carrier liquid and contact surface for diazinon to transfer efficiently.

It is important to interpret this finding carefully. The 20:100 ratio resulted in the highest extraction efficiency but did not indicate the highest stripping efficiency nor the minimum membrane breaking. The efficiency of stripping was 92.41% at 20:75 and the breakage of membrane was 1.4%. Stripping efficiency was, however, 80.25 % with a slight rise in membrane rupture at 20:100 at 20:100. This means that the best ratio will vary according to the answer chosen. If the primary objective is the removal of the highest amount of diazinon from the external aqueous phase, the condition of 20:100 is most favorable. Using 20:75 is more desirable if internal recovery and stability of the membrane are considered.

The lower extraction efficiency at 20:50 could be explained by the higher emulsion fraction, which would have caused an increase in the viscosity of the emulsion, and a reduction in the amount of emulsion globules that had contact with the external diazinon solution. Lowering the ratio to 15:100 brought extraction efficiency down to 84.35%, exposing a capacity constraint in which the reduced volume of carrier liquid and stripping agent could not handle the full pesticide load present in the external phase.

Operational trade-offs are common in ELMs. Using higher emulsion volume increases extraction by increasing the mass of membrane phase and the surface area of the interface, but may also affect dispersion quality, swelling properties and phase separation. The sensitivity of ELM performance to a phase ratio and membrane stability observed in previous ELM studies (Al-Damluji & Mohammed, 2023; Hussein et al., 2019) is also observed in this study.

Thus, ratio of 20:100 was chosen as the optimum ratio for maximum extraction, to achieve the highest diazinon removal from the external phase. This condition is not necessarily optimal for all of the performance criteria, however, as the optimum value for stripping efficiency and membrane stability was found at 20:75.

Fig. 11. Influence of the emulsion-to-external phase ratio on diazinon extraction efficiency, stripping efficiency, and membrane breakage, with error bars denoting standard deviations across triplicate experiments (n = 3).

3.8. Diazinon Extraction Kinetics

An apparent first-order kinetic model served to assess the extraction kinetics governing diazinon removal. The graph of $(-\ln(C/C_0))$ versus time was almost linear, as can be seen in Fig. 12, with a slope of 0.3081 min^{-1} and correlation coefficient (R^2) of 0.9962. This suggests that diazinon extraction could be reasonably modeled by an apparent first-order kinetic model at the conditions used. The reaction rate equation is:

$$-\ln\left(\frac{C}{C_0}\right) = k_{obs} t \quad \dots(6)$$

where C_0 = initial concentration of diazinon in the external phase,

C = the concentration of diazinon in the external phase at time t ,

K_{obs} = the apparent extraction rate constant.

The kinetic behavior is like that for the extraction mechanism that is used in the present ELM system. An initially steep concentration gradient of diazinon between the external and membrane phases produces a strong driving force, enabling rapid transport of diazinon across the interface. During the extraction, the external phase's diazinon concentration drops, and the driving force for transport gets lower. Thus, the first-order behavior observed is an overall result of the decline in diazinon levels in the feed phase, not any rate-limiting step.

The value of (k_{obs}) should be understood as an overall kinetic parameter for the whole transport process. The external phase to emulsion surface diffusion, the partitioning to the membrane phase (xylene), the transfer through the membrane and the stripping into the internal phase (HCl). Therefore, the first order model can be used as an effective model for the extraction rate and the good linear trend ($R^2 = 0.9962$) shows good stability and uniformity of the diazinon transfer under the selected operating conditions. The same apparent first-order kinetic behavior was reported in ELM systems by measuring the decrease in the concentration of the solute in the external phase instead of measuring the rate of any elementary reaction step (Mohammed & Al-Khateeb, 2022) (Kohli et al., 2019).

Fig. 12. Apparent first-order extraction kinetics of diazinon using the H-SiO₂/TiO₂-assisted emulsion liquid membrane system

3.9. Recyclability of the Membrane Material

The recyclability test demonstrated that the extraction capacity of the membrane supported by H-SiO₂/TiO₂ decreased significantly in the initial reuses but gradually continued to decrease with subsequent reuses. The extraction efficiency was found to be 93.25, 90.12, 86.85 and 83.24% for original run, 1st, 2nd and 3rd cycle, respectively as shown in Fig. 13. The stripping efficiencies also showed a similar decline, from 90.23% to 88.23%, 83.47% and 80.15% on the same cycles. A steady decrease indicates that the membrane phase didn't lose its function in the first three reuses, but that there was already some loss of transport efficiency.

A higher reduction was seen in the 4th and 5th cycles. The extraction efficiency reduced to 73.58% and 64.57% and stripping efficiency decreased to 70.44% and 60.27% respectively. This decrease is probably due to some saturation of the membrane phase by the remaining diazinon, loss and/or aggregation of the H-SiO₂/TiO₂ nanoparticles and changes in the interfacial film of Span 80 upon repeated demulsification and re-emulsification. These decreases decrease the effective interfacial area and impair the functionality of the membrane in transferring diazinon from the external aqueous phase to the internal stripping phase.

It was found that the membrane system proved reusability; however, extended recycling requires regeneration strategies in order to maintain its extraction performance. Generally the first three cycles demonstrated satisfactory performance retention while cycle 4 and 5 demonstrated significant loss of extraction and stripping efficiency. These increase in the swelling, leakage, coalescence and degradation of emulsion stability have been correlated with the decline in reused ELM systems during repeated operation (Kusumastuti et al., 2020). The result is that the membrane phase should be regenerated or that the concentration of Span 80 should be adjusted or that the concentration of the nanoparticle stabilizer should be replenished, if extended use is desired in order to sustain the extraction performance.

Fig. 13. Recyclability of the H-SiO₂/TiO₂-assisted membrane for diazinon extraction and stripping during repeated uses. Error bars are the standard deviation of the triplicates (n = 3).

3.10 Study Limitation Related to Control Experiments

Optimized H-SiO₂/TiO₂-assisted ELM system exhibited high diazinon extraction efficiency, but there was no separate control experiment included in the present study. Specifically, the experiments for which ELM was not used, as well as for experiments in which ELM is used but no H-SiO₂/TiO₂ nanoparticles, and for direct adsorption experiments using nanoparticles without ELM, were not conducted. Hence, it was not possible to separate quantitatively the contribution that each of the different components of the adsorption, surfactant stabilization and nanoparticle-assisted interfacial stabilization could make. These control experiments should be repeated in future investigations to gain a better understanding of the mechanisms involved in diazinon transport and to better understand the individual contribution of each ELM component.

4. Conclusion

The present study examined the diazinon removal from synthetic aqueous solutions via a Hibiscus assisted SiO₂/TiO₂-stabilized emulsion liquid membrane system. Results indicate that the extraction of diazinon was controlled by both mass transfer and emulsion stability. Favorable conditions promoting dispersion and intimate contact between the droplets facilitated removal, while high shear, high internal acidity, excess surfactant or excess loading of the nanoparticles led to decreased removal through weakening of the membrane structure or through increased resistance to solute transport.

The external pH of the phase was 7, homogenizer speed was 5800 rpm, emulsification time was 6 min, HCl concentration was 0.15 M, stirring speed was 250 rpm, Span 80 concentration was 2% v/v, and H-SiO₂/TiO₂ dosage was 0.4 mg within the tested range. The emulsion to external phase ratio of 20:100 gave the highest extraction of diazinon from the external phase (96.35%). The ratio of 20:75, however, was more effective at stripping and experienced lower membrane breakage. It means that for the selected response (maximum removal, internal recovery or membrane stability), there is an optimum operating condition.

According to the results of the recycling test, the membrane had good extraction performance up to the third cycle, but it declined dramatically in the fourth and fifth cycles. This loss is most likely attributed to the partial aggregation or loss of the nanoparticles and deterioration of the interfacial film formed by Span 80 during repeated demulsification and re-emulsification. Hence, though the membrane system can be reused, the improvement of membrane regeneration and emulsion reconstruction is needed before long-term repeated operation can be achieved.

The H-SiO₂/TiO₂-assisted ELM system showed great promise for removing diazinon from aqueous solutions. Further validation using real agricultural or industrial wastewater containing competing ions, dissolved organic matter, suspended solids, and variable pH conditions.

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Table 1. Experimental parameter ranges investigated in this study.

Range of pH	(3, 7, 10)
Homogenizer speed, rpm	3000, 5800, 12700
Emulsified time, min	2,4,6,8,10
Span 80 concentration, % v/v	1, 2, 3
Concentration (HCl), mol/L	0.05, 0.15, 0.5
Dosage of H-TiO₂ /SiO₂(mg)	0.2, 0.4, 0.6
Stirrer speed, rpm	150, 250, 350
Emulsion to external ratio, mL/mL	20:50, 20:75, 20: 100, 15:100.

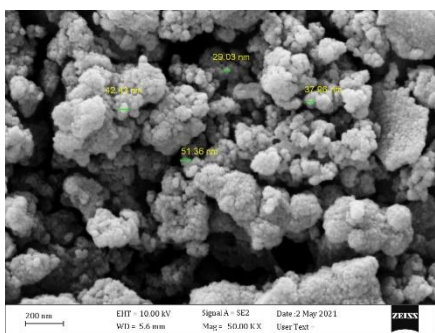


Fig. 1.a: SEM photos of H-TiO₂/SiO₂ Before treatment at 200nm magnification

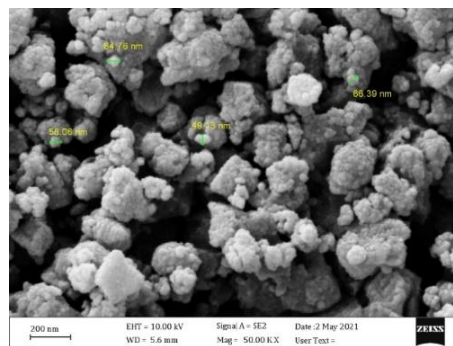


Fig. 1.b: SEM photos of H-TiO₂/SiO₂ after treatment at 200nm magnification

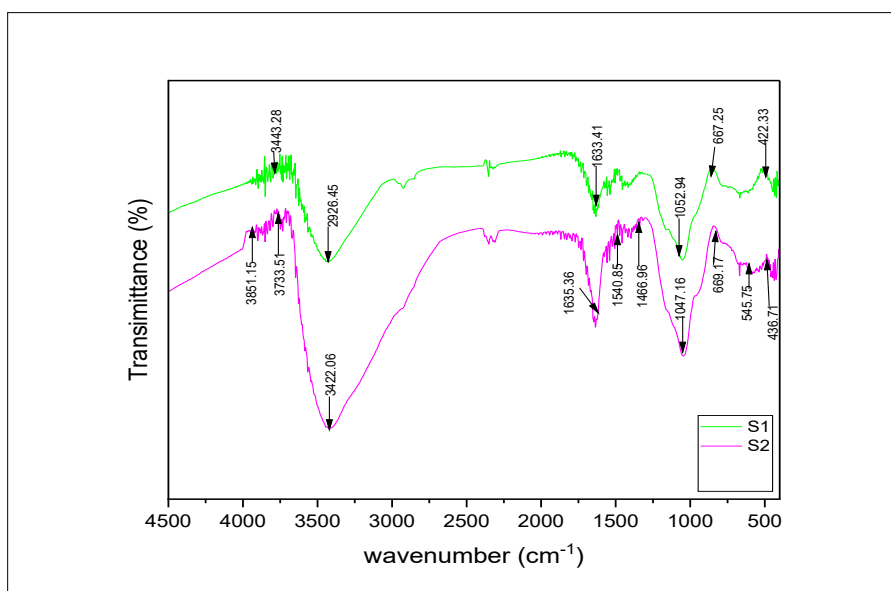


Fig. 2: Transformation of FTIR Spectrum of H-TiO₂/SiO₂ Nanoparticles Following Treatment

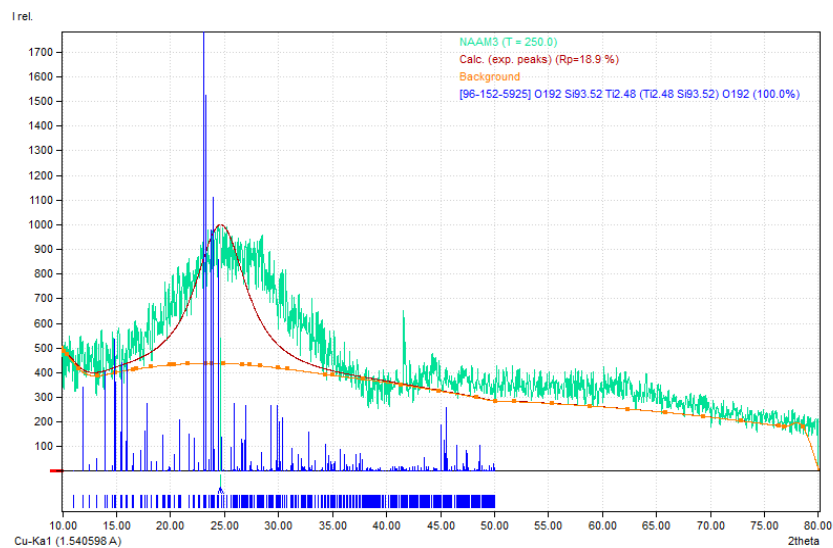


Fig. 3: XRD patterns of H-TiO₂ /SiO₂ nanocomposites.

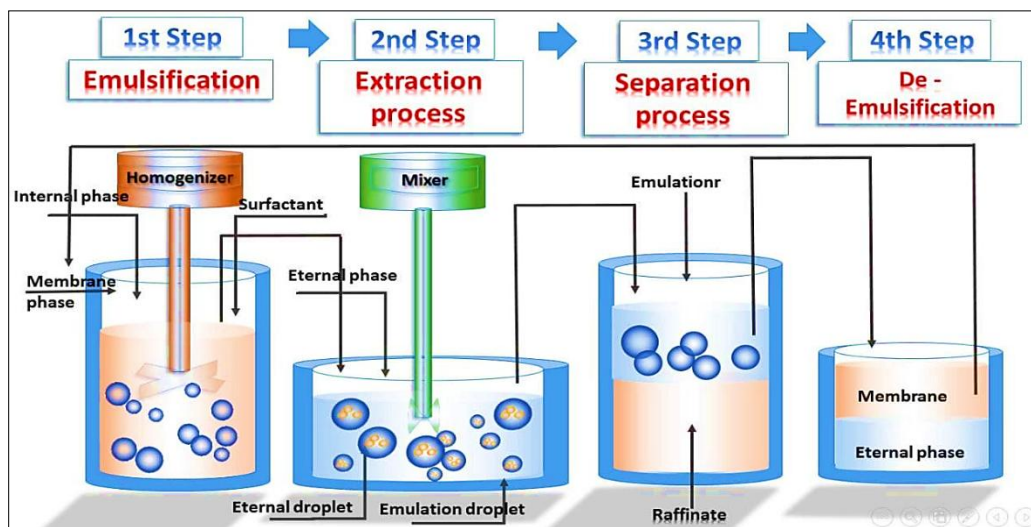


Fig.4: diagram of the emulsion procedure

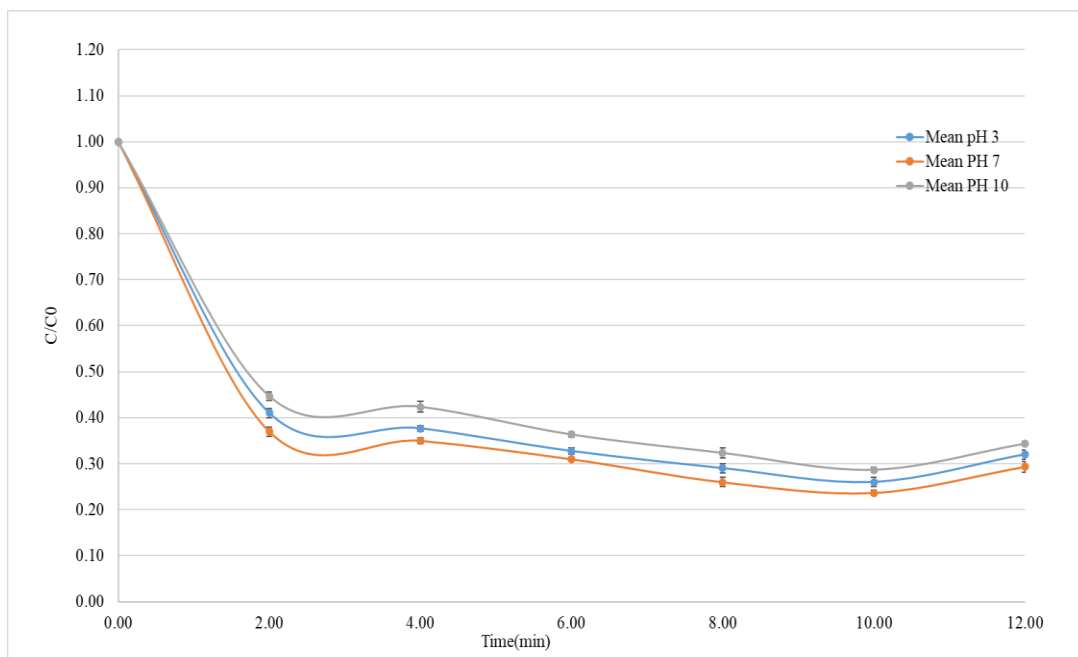


Fig.5: Normalized diazinon concentration (C/C_0) during extraction with H-SiO₂/TiO₂-assisted emulsion liquid membrane system as the external phase pH was changed. Error bars are shown as standard deviation of the triplicates (n = 3).

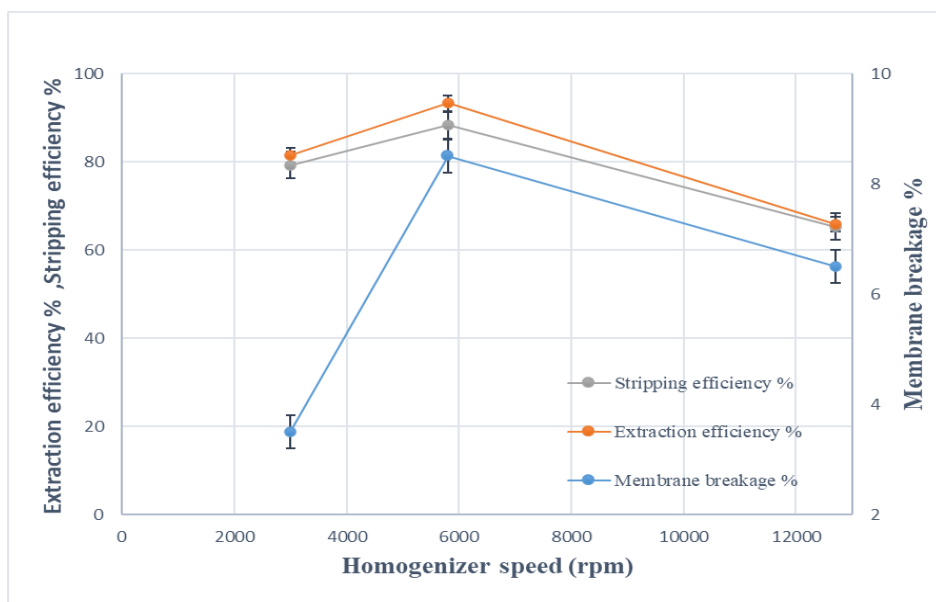


Fig. 6.a. Effect of homogenizer speed on diazinon extraction efficiency, stripping efficiency, and membrane breakage by H-SiO₂/TiO₂-assisted emulsion liquid membrane system.

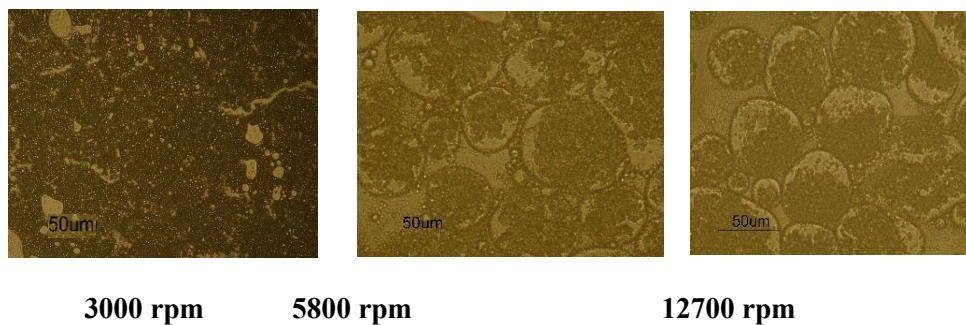


Fig. 6.b. Optical microscopy images of the W/O emulsion droplets from different homogenizer speeds.

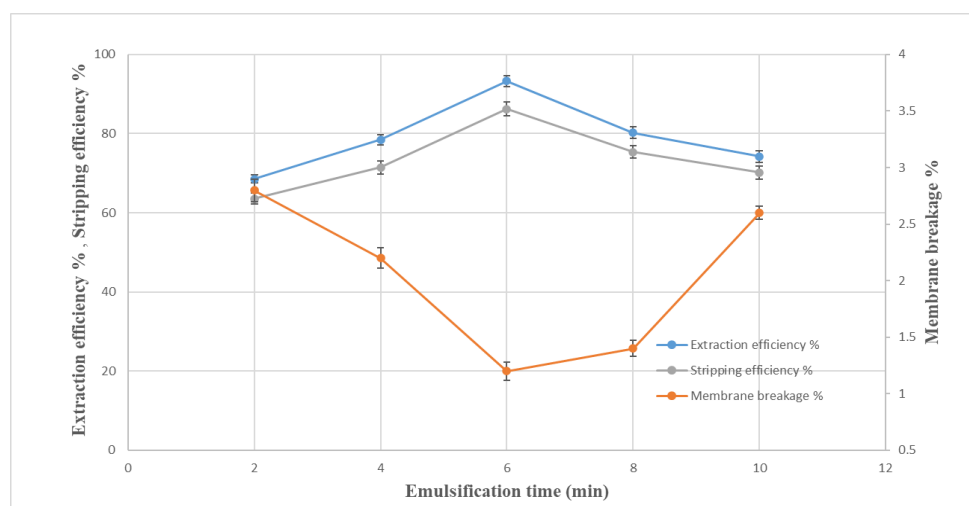


Fig. 7. Effect of emulsification duration on diazinon extraction and recovery within the H-SiO₂/TiO₂-assisted emulsion liquid membrane system, derived from triplicate measurements (n = 3).

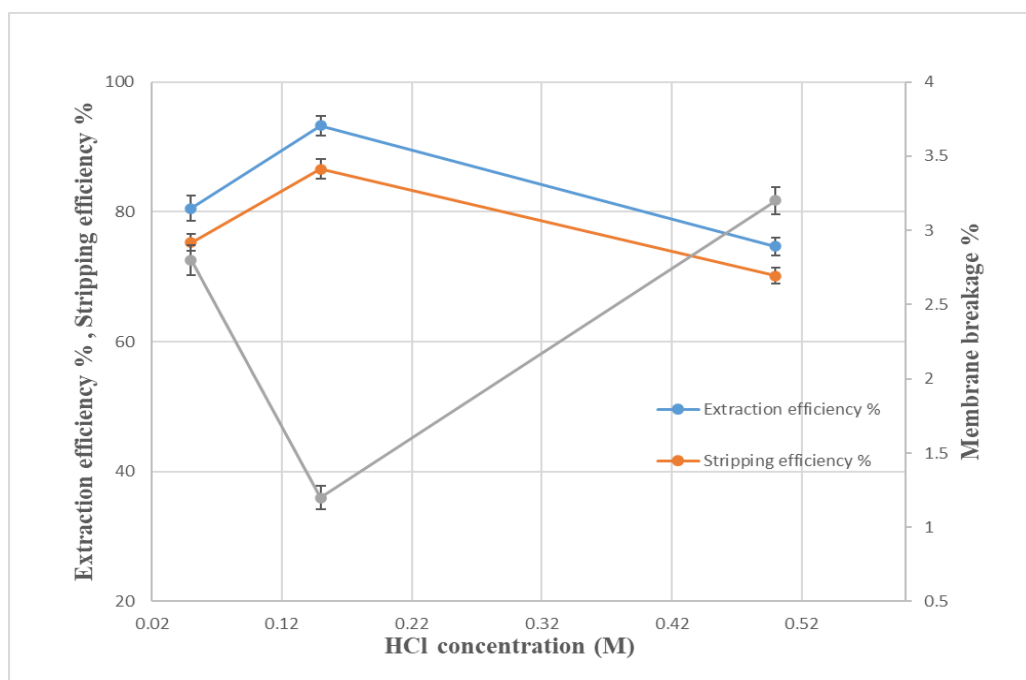


Fig. 8. Influence of HCl concentration on diazinon extraction, stripping efficiency, and membrane breakage within the H-SiO₂/TiO₂-assisted emulsion liquid membrane system.

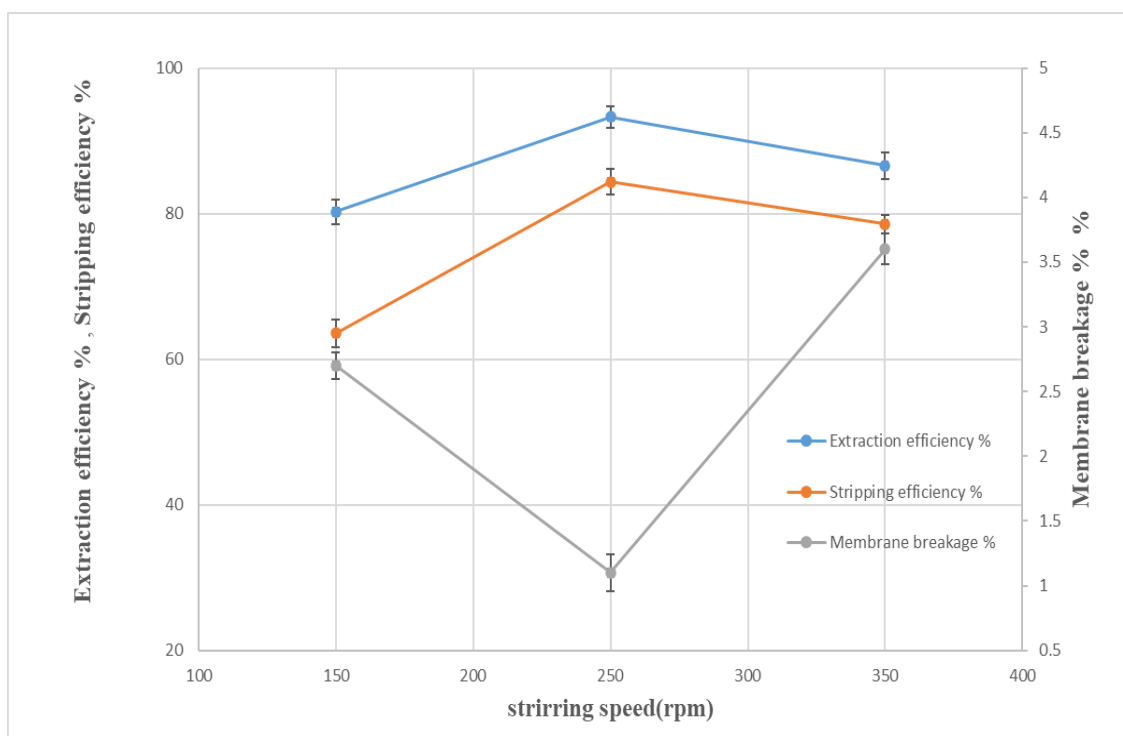


Fig. 9. Diazinon extraction efficiency, stripping efficiency, and membrane breakage as a function of stirring speed using the H-SiO₂/TiO₂-assisted emulsion liquid membrane system. Three triplicate measurements ($n = 3$) were used to calculate the standard deviation.

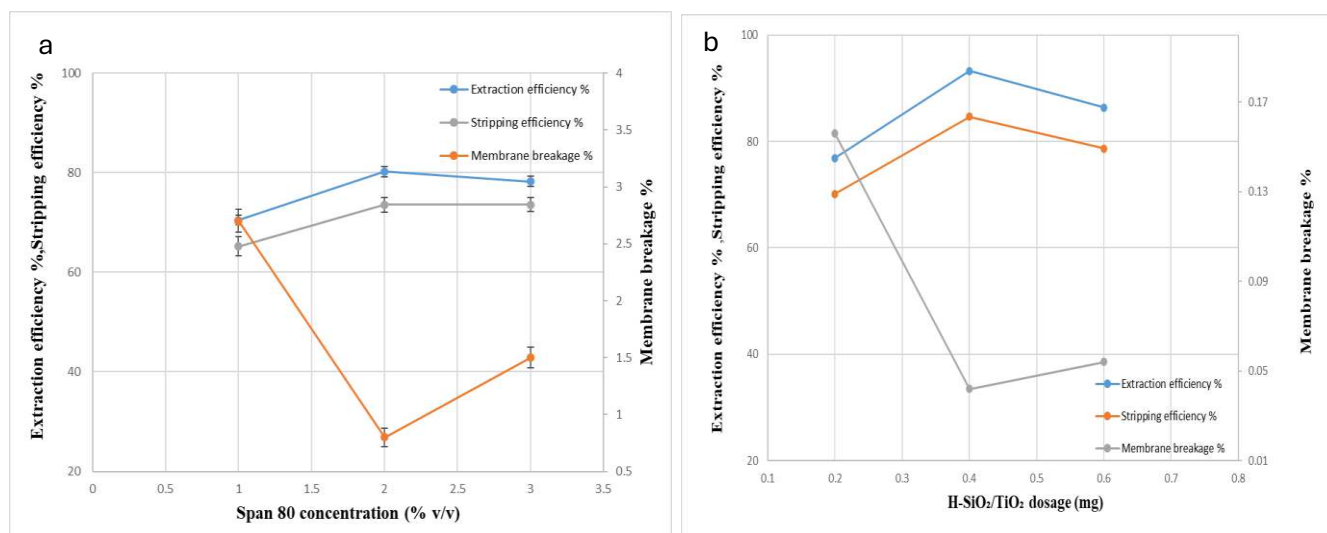


Fig. 10. Effect of (a) Span 80 concentration and (b) H-SiO₂/TiO₂ nanoparticle dosage on extraction efficiency, stripping efficiency, and membrane breakage.

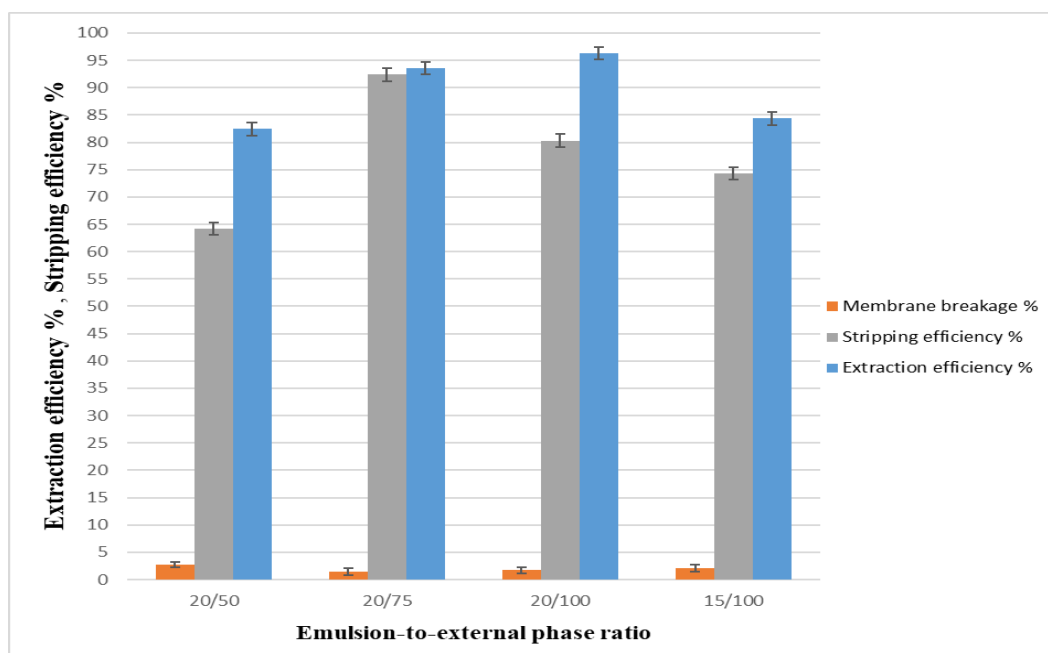


Fig. 11. Influence of the emulsion-to-external phase ratio on diazinon extraction efficiency, stripping efficiency, and membrane breakage, with error bars denoting standard deviations across triplicate experiments (n = 3).

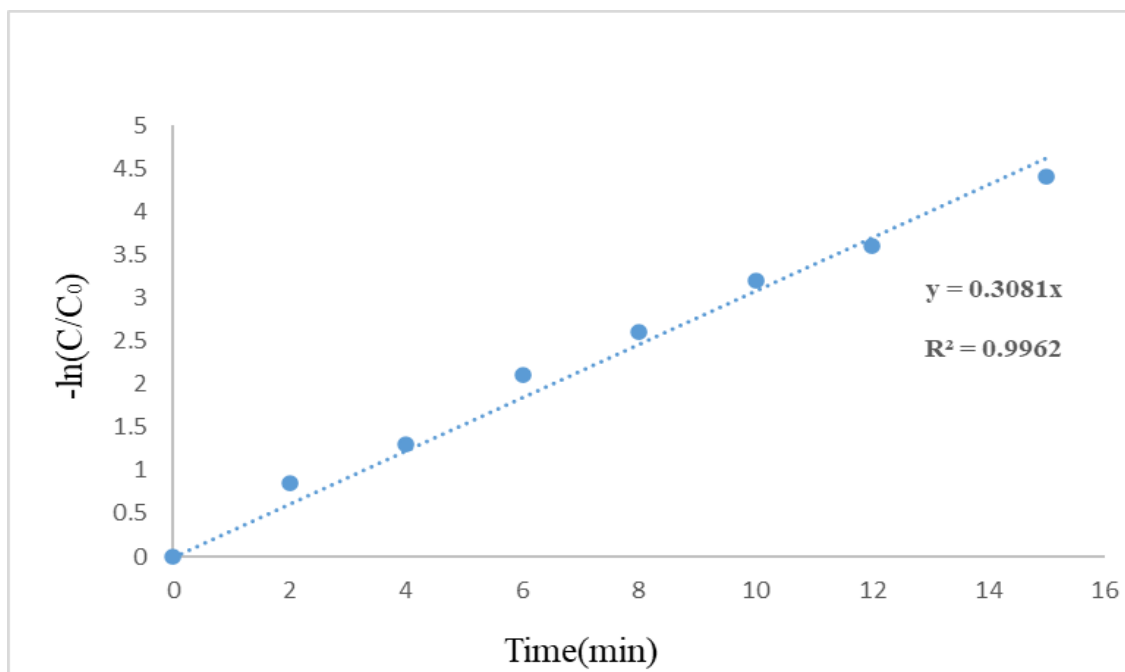


Fig. 12. Apparent first-order extraction kinetics of diazinon using the H-SiO₂/TiO₂-assisted emulsion liquid membrane system

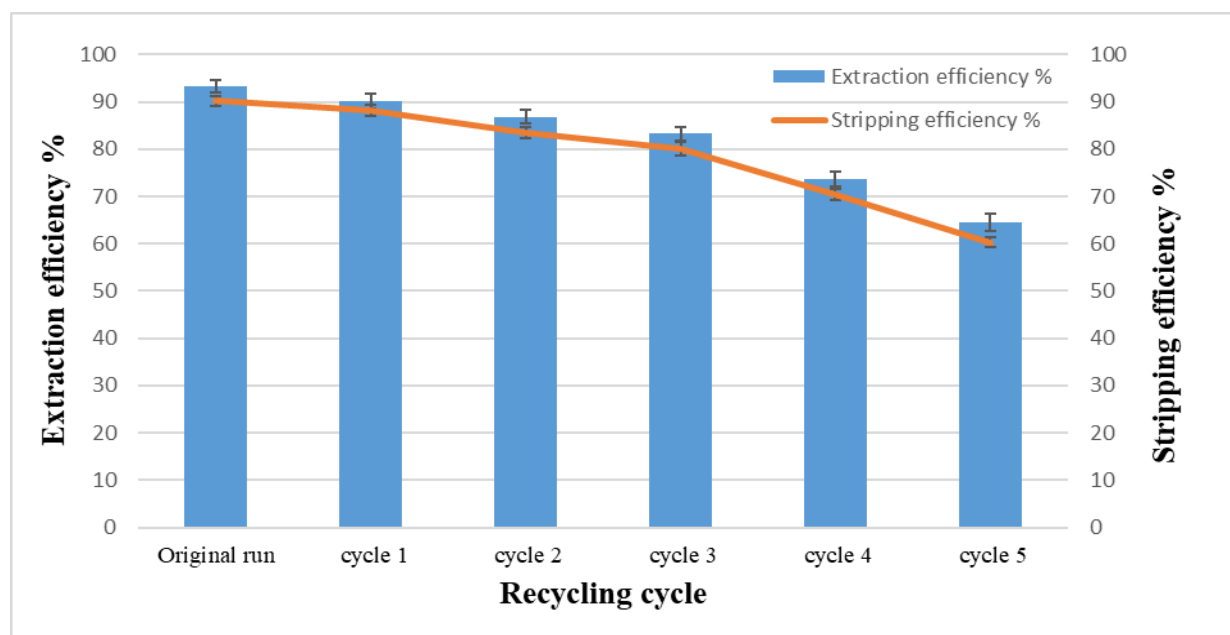


Fig. 13. Recyclability of the H-SiO₂/TiO₂-assisted membrane for diazinon extraction and stripping during repeated uses. Error bars are the standard deviation of the triplicates (n = 3).

