Natural deep eutectic solvents for turbidity removal from synthetic pharmaceutical wastewater

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Abstract

Contamination of water resources by active pharmaceutical ingredient wastes is among major environmental concerns. To prevent major disruptions of aquatic life, an efficient and environmentally-friendly turbidity removal procedure of common contaminants such as paracetamol should be established. In this study, several natural deep eutectic solvents (NADESs) were screened to reduce the turbidity of simulated water contaminated with paracetamol below the standard turbidity limit recommended by the National Water Quality Standards for Malaysia (50 NTU). The optimal operating parameters (NADES dosage, stirring time and operating pH) were determined. Under optimized conditions, stearic acid-based NADES achieved the highest turbidity removal of 97.5 %. High coagulation performances were investigated based on molecular interaction using COSMO-RS (COnductor like Screening MOdel for Real Solvents) σ-profile and σ-potential (histogram of charge density distribution over molecular surface) and showed high affinity between the NADES compounds and paracetamol. Thus, NADESs are promising candidates for turbidity removal of paracetamol from water and are viable in further investigations for effluent treatment applications.

Keywords: Active pharmaceutical ingredients; flocculation; coagulation; wastewater treatment.

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1. INTRODUCTION

Substantial efforts in research and industrialisation have been carried out to establish effective treatment and purification of industrial wastewater to meet the increasing public demand of clean water. These efforts include various techniques which were conducted for removal of pollutants from wastewater with high efficiency such as liquid-liquid extraction (LLE), aqueous biphasic systems, adsorption, and application of liquid membranes [1-3]. Wastewater treatment plants usually involve physical, chemical, and biological treatments to minimize and remove pollutants from water. Individual wastewater treatment methods that are classified as primary, secondary and tertiary treatment methods are integrated into a set of systems to achieve a certain degree of contaminant elimination [4]. Industrially, the treatment of wastewater utilizes numerous chemical substances such as activated carbon, chlorine, ozone, and ionic

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liquids (ILs) [5]. However, such chemical substances pose challenges in terms of manufacturing/operating costs, material reusability and recyclability, and environmental impact during disposal when exhausted [6]. Therefore, further studies are required towards development of advanced water purification processes using sustainable, renewable low-cost materials.

Importance of utilization of natural deep eutectic solvents (NADESs) in extraction of pollutants from wastewater has been widely explored in numerous studies such as purification of water contaminated with bisphenol-A (BPA) using hydrophobic deep eutectic solvents (DESs) [7], a circular approach to purify water contaminated with ciprofloxacin by using hydrophobic DESs [8], synthesis and characterization of DESs and hydrophobic application for micro-extraction of environmental water samples [9], development of hydrophobic DESs for extraction of pesticides from aqueous environments [10] and separation and pre-concentration of parabens from water samples by liquid-liquid micro-extraction [11]. The outcomes of these studies reveal that DESs are one of many viable and effective alternative materials in removing pollutants of high concern, such as BPA, pesticides and active pharmaceuticals ingredients (APIs) from wastewater. However, the ability of DESs to remove turbidity of wastewater induced by paracetamol content has not been studied yet despite its exacerbating impact towards the environment due to the increased production and consumption by humans.

In this study, NADESs are employed as cost-effective materials acting as the coagulant stage in API wastewater treatment. Specifically, NADESs were studied as alternative solvents regarding the ability to decrease the turbidity of water contaminated with paracetamol to below the standard turbidity limit recommended by the National Water Quality Standards for Malaysia (50 NTU). The optimal conditions were achieved by manipulating experimental parameters such as the dosage of NADESs, stirring time and pH of the water system. Furthermore, the interactions between the NADES constituents and paracetamol were investigated and inferred using COSMO-RS. Ultimately, this study demonstrates DESs as a viable and effective alternative in water purification technologies by method of extraction of pollutants.

2. MATERIALS AND METHODS

NADESs were synthesised from the following chemical constituents: stearic acid (SA, Merck, Malaysia, ≥97 %), levulinic acid (LA, Sigma Aldrich, Malaysia, ≥98 %), malonic acid (MA, Sigma Aldrich, Malaysia, ≥99 %), and choline chloride (ChCl, Sigma Aldrich, Malaysia, ≥98 %). Synthetic wastewater samples contaminated with acetaminophen (paracetamol, Merck, Malaysia, ≥99 %) were prepared by dissolving paracetamol in distilled water yielding an acetaminophen solution of 10 g L^{-1} concentration. An electronic turbidity meter (HI 98703, Hanna Instruments, Woonsocket RI, USA) was used to measure the initial and final turbidity readings of the synthetic wastewater. The solution pH was adjusted by adding either 0.1 M sodium hydroxide solution or 0.1 M hydrochloric acid solution, and was measured using a digital pH meter (Mettler Toledo Seven Compact, Switzerland).

2. 1. Preparation of NADESs

NADESs were prepared according to similar procedures published in prior literature [12]. Briefly, the NADESs were prepared by mixing a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) constituent at specific component molar ratios as listed in Table 1. The obtained mixtures were stirred vigorously at 60 – 65 °C using a hot plate magnetic stirrer until a homogenous liquid is formed.

Table 1. Molar ratios of chemical constituents used to prepare the NADESs, hydrogen bond acceptor is choline chloride

Hydrogen bond donor (HBD)	Molar ratio	Abbreviation of NADES
Stearic acid (SA)	1:2	ChCl:SA
Malonic acid (MA)	1:1	ChCl:MA
Levulinic acid (LA)	1:2	ChCl:LA

2. 2. Optimisation of experimental parameters

The list of NADESs prepared in Table 1 and its individual constituents were screened as natural coagulants for turbidity removal, and the compounds with acceptably high efficiency in turbidity removal were selected for further optimisation.

The dosage of NADESs was optimised as follows: initially, 2 g of NADESs were added to 500 mL of simulated wastewater at pH 6.0. Flash mixing mode (coagulation) was first performed at a stirring rate of 200 rpm for 5 min. Subsequently, slow mixing at a stirring rate of 150 rpm was conducted for 15 min. After the stirring procedures, the treated wastewater was allowed to sit for 30 min, at which the treated wastewater was sampled by pipetting a sample out from the beaker at a predetermined depth below the water surface. The final turbidity reading was recorded by using the turbidity meter. The experiment was conducted in triplicates to obtain the average value. The experimental procedures were repeated with different increasing dosages of NADESs (10, 16, 20 and 40 g L^{-1}). The coagulation efficiency is represented by the turbidity removal efficiency (TRE) from wastewater and is calculated based on equation (1):

$$\text{TRE}=\frac{T_0-T}{T_0}100 \tag{1}$$

where T_0 is the turbidity of paracetamol-contaminated wastewater before extraction and T is the turbidity of paracetamol-contaminated wastewater after extraction.

Optimisation of stirring time was conducted by using the optimised dosage of NADESs on turbidity removal. The effect of stirring time was investigated for 10, 15, 25 and 30 min. Finally, the optimal pH of the wastewater system was investigated for pH 4, 7, 9 and 11 using the pre-determined optimum conditions of NADES dosages and stirring time.

3. RESULTS AND DISCUSSION

3. 1. Screening of NADESs as potential coagulants

Screening of NADESs and its individual constituents was conducted prior to the optimisation step and the results are presented in Figure 1. At the pre-optimisation stage, the highest turbidity reduction was achieved by ChCl:SA (90 %), followed by ChCl:LA (85 %) and ChCl:MA (84 %). Additionally, the individual organic acid constituent of the NADESs exhibited some level of performance in turbidity removal. For example, LA as a standalone compound achieved a TRE of 77 %, whereas MA achieved the lowest TRE value out of the three acid constituents at 57 %. In the further optimisation analysis, the individual constituents were excluded from further optimisation based on the turbidity removal performance of the NADESs. The NADESs were used as new coagulants for the turbidity removal of simulated wastewater samples contaminated with paracetamol.

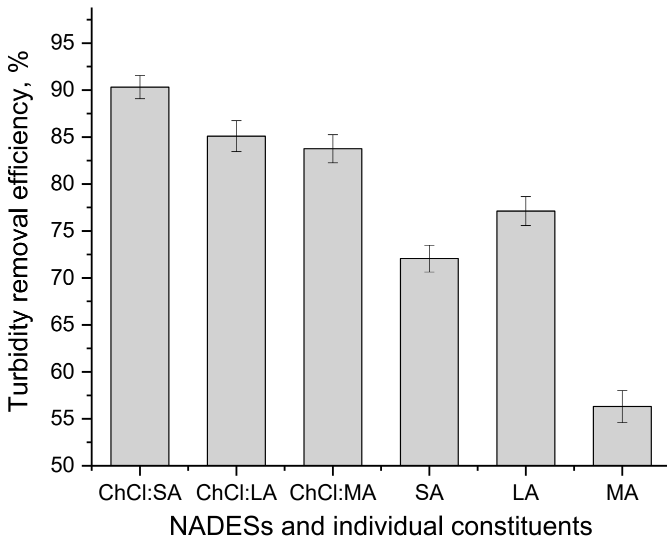

Figure 1. Screening of NADESs and its individual constituents in relation to its turbidity removal performance (data are average of n=3)

3. 2. Dosage effect of NADESs

The effect of NADES dosages on the turbidity removal is shown in Figure 2. Each NADES resulted in different optimum dosages that efficiently reduced turbidity of the wastewater. The optimum dosage of ChCl:SA NADES was determined as 16 g L^{-1}, where the turbidity reading of the wastewater was decreased from 400 NTU to 10 NTU, corresponding to a TRE of 97 %. On the other hand, the ChCl:LA NADES achieved a high TRE value of 94 % at the lowest optimum dosage among the three NADESs at 10 g L^{-1}. Comparatively, ChCl:MA NADES required the highest optimum NADES dosage of 20 g L^{-1} to achieve 96 % TRE. The optimum dosage depends on the coagulant's molecular weight, ionic character and degree of ionization. Ultimately, low coagulation and flocculation efficiencies are due to the insufficient or excessive dosages of DESs. Larger dosages could either agitate the sedimentation process causing re-suspension of aggregated particles [13].

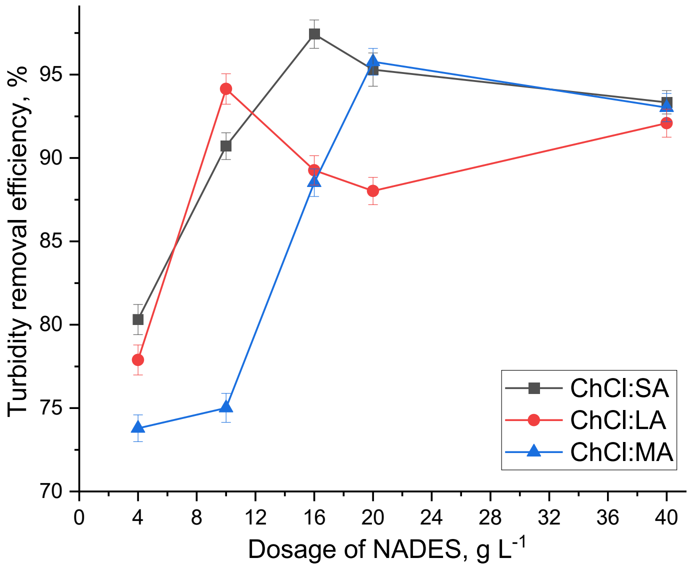

Figure 2. Effect of NADES dosage on turbidity removal efficiency of synthetic paracetamol contaminated wastewater (data are average of n = 3)

3. 3. Effects of stirring time

Effects of stirring time on the turbidity removal are presented in Figure 3. For the ChCl:SA NADES, the optimum stirring time was determined at 20 min where the turbidity decreases from around 400 NTU to 11 NTU, corresponding to a TRE value of 97 %.

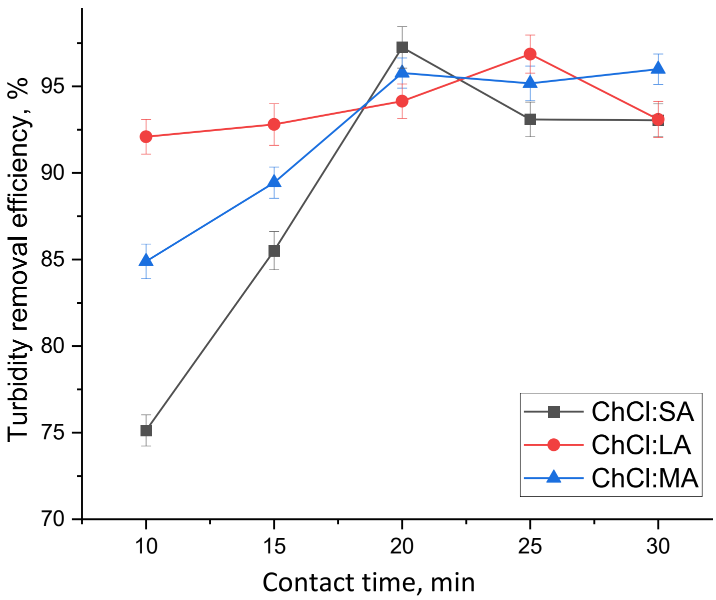

Figure 3. Effect of stirring time on turbidity removal efficiency of synthetic paracetamol contaminated wastewater using optimized NADES dosages (data are average of n = 3)

Similar TRE performances can be achieved by using the ChCl:LA NADES at the optimum stirring time of 25 min. The ChCl:MA NADES achieved a maximum of 96 % TRE at the optimal stirring time of 30 min, which was the longest stirring time out of the three NADESs investigated. In the present study, the coagulation and flocculation steps are assumed to occur in stages and the stirring time was observed to affect both processes. However, the coagulation is unaffected by excessive mixing, but inadequate mixing can result in the incomplete coagulation phase. Typically, the contact time for rapid-mixing is allowed for 1–3 min, while the design of flocculation contact times may vary from 15–60 min according to the equipment design.

3. 4. Effects of pH of the wastewater system

Effects of the solution pH on the turbidity removal are shown in Figure 4. The optimum pH for stearic acid and levulinic acid-based DES is pH 6 where the turbidity level can be reduced from around 400 NTU to 11 NTU and 13 NTU. pH 7 was the optimal pH value for the turbidity removal using ChCl:MA where the turbidity was reduced from around 400 NTU to 16 NTU. Hence, it can be concluded that choline chloride-based deep eutectic solutions can perform well in the pH range of 6-7. The surface charge of the coagulants is affected by the pH of the water. The surface of coagulated paracetamol particles is negative at high pH, resulting in a lower turbidity removal. When H^+ ions are added, pH steadily decreases with the turbidity, resulting in a relatively clear supernatant. This is due to the increasing concentration of hydrogen ions in the suspension which neutralises some of the negative charges on the coagulated paracetamol particles [14].

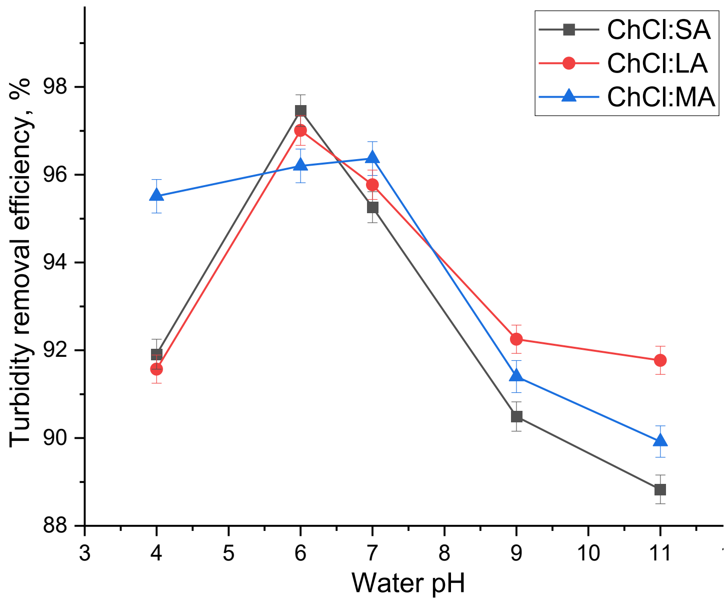

Figure 4. Effects of wastewater pH on turbidity removal efficiency using optimized NADES dosages and stirring time (data are average of n = 3)

3. 5. Performance comparison of NADESs under optimal conditions

Turbidity removal efficiencies of the NADESs and their individual constituents at the optimised conditions are illustrated in Figure 5. The optimized NADES dosage, stirring time and water pH of each NADES employed in this study are presented in Table 2. The highest turbidity reduction was achieved by ChCl:SA (97.5 %), followed by ChCl:LA (97.0 %) and ChCl:MA (96.4 %). The NADES constituent components were also efficient in removing the turbidity of wastewater with the turbidity reduction efficiency ranging from 87 to 93 %. Similar trends were observed at the screening stage, where malonic acid alone was less efficient in the turbidity removal compared to stearic and levulinic acids at their optimal conditions. Comparatively, the effects of various ChCl-based NADESs were previously studied for the turbidity removal in a bentonite suspension [13,14]. Carboxylic acids such as citric, lactic and malic acids were used as the HBD components of the NADESs revealing high removal efficiencies of up to 100 %. The results from this study showed comparable removal efficiencies with NADESs based on other types of carboxylic acids as their constituents. Furthermore, these results suggest that the fatty acids alone could perform well in removing turbidity.

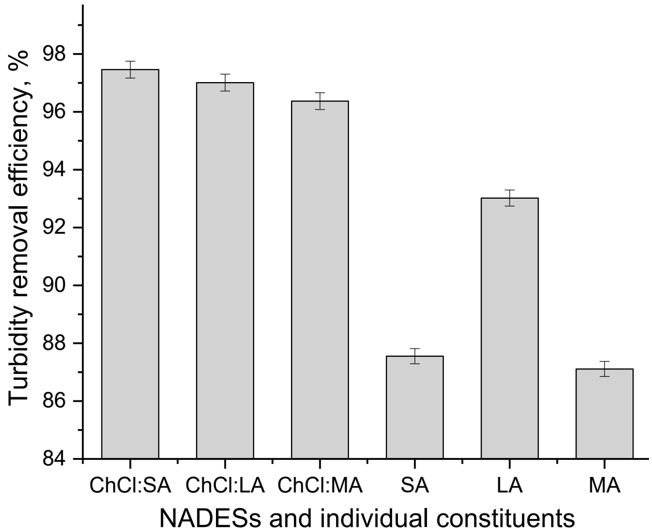

Figure 5. Comparison of turbidity removal efficiencies of NADESs and their individual constituents under optimal conditions (data are average of n = 3)

Table 2. Optimized NADES dosage, stirring time and wastewater pH for the removal of turbidity in paracetamol contaminated wastewater

	ChCl:SA	ChCl:LA	ChCl:MA
Dosage, g L^{-1}	16	10	20
Stirring time, min	20	25	30
pH of water system	6	6	7

3. 6. Investigation of molecular interactions between the pollutant and NADES

The performance of coagulants in this work can be explained by interactions between molecules with respect to the COSMO-RS σ-profile and σ-potential (histogram of charge density distribution over molecular surface). The validity of this approach was explained in detail in literature [15] and was reported in many recent studies involving molecular interactions analysis [16-18]. In the σ-profile, the molecule is considered adequately polar to induce hydrogen bonding as the screening charge density exceeds ±0.84 e nm^{-2}. A higher σ absolute value shows that the compound is a stronger HBD or HBA. On the other hand, the σ-potential indicates affinity of a component in a mixture towards another. In the σ-potential plot, a higher negative μ (σ) value indicates enhanced attraction between the molecules, whereas a higher positive value indicates increased repulsion between the molecules. In the horizontal axis, an increase in the negative and positive values for the hydrogen bonding threshold (±0.84 e nm^{-2}) indicates the region of a molecule where interactions between the HBDs and HBAs occur, respectively. The σ-profile and σ-potential of all species involved in this study are depicted in Figures 6 and 7, respectively.

In the turbidity reduction process, the coagulation mechanism can be inferred from interactions between paracetamol and the coagulants. Firstly, it is relevant to observe solvation effects in a mixture of paracetamol and water. As seen in Figure 6, water molecule possesses both donor and acceptor abilities via the hydrogen bonding between hydrogen atoms and the oxygen atom, respectively. Paracetamol possesses several peaks in the non-polar region due to the presence of the benzene ring and methyl group within the molecular structure. Additionally, paracetamol also exhibits peaks in the polar regions, which may be responsible for the hydrogen bonding with water observed from the similar peaks in the σ-profile of water. However, the non-polar surface of paracetamol makes it sparingly soluble in water at ambient temperature. Therefore, a competition can be expected between the water–paracetamol interaction and their corresponding self-associations, *i.e.* water–water and paracetamol–paracetamol interactions.

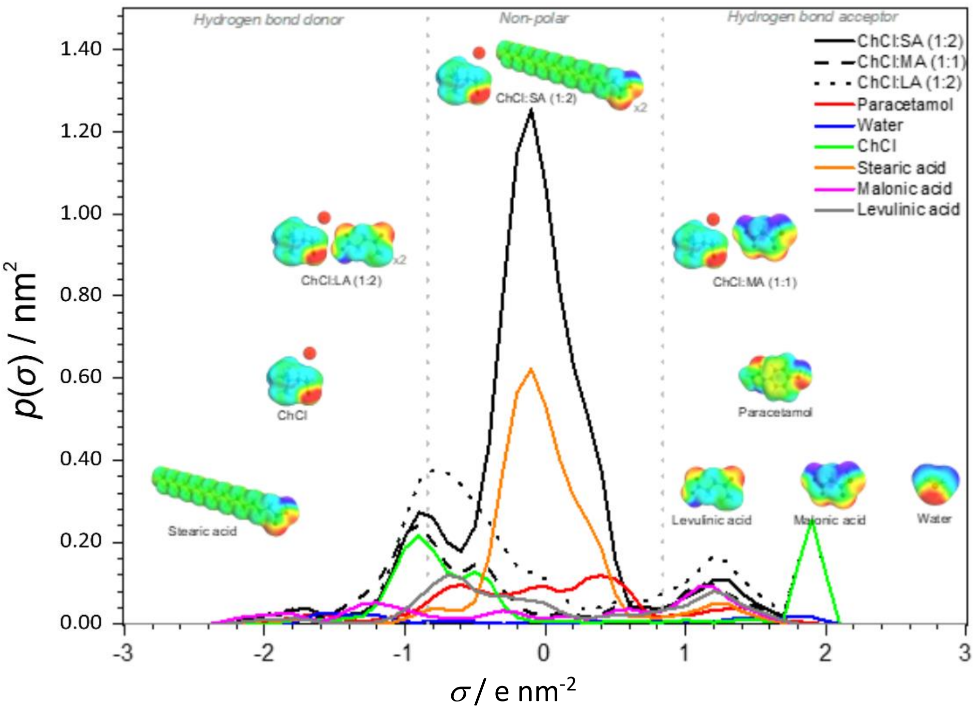

Figure 6. Plot of σ-profiles for the NADESs and their individual constituents, paracetamol, and water

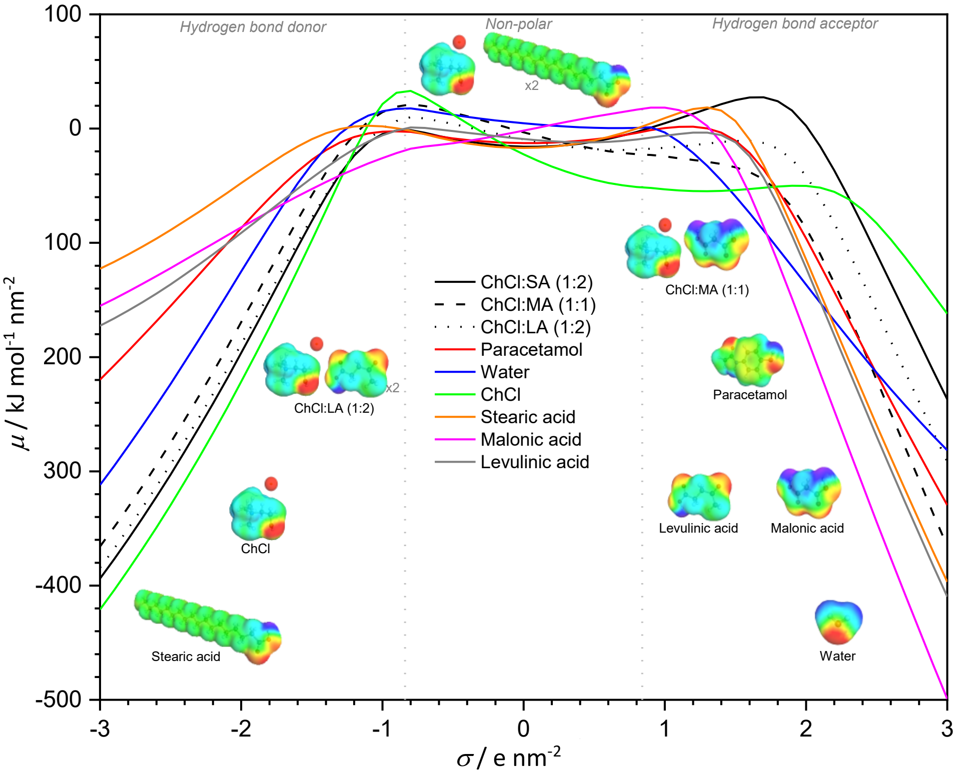

Figure 7. Plot of σ-potentials for the NADESs and their individual constituents, paracetamol, and water

From the paracetamol accumulation in water, a net negative charge can be expected from the colloids as paracetamol has more peaks in the hydrogen bond acceptor region. This explains the coagulation effect from the neutralization of opposite charges upon the introduction of coagulants, and consequently decreasing the turbidity of water. This also suggests that the coagulant should have high hydrogen bond donor ability or being highly electronegative *i.e.* exhibiting the peaks or the curve in the left side of the σ-profile. The σ-potential of both molecules also explains similar molecular interactions, where the interactions occur mainly in the polar regions.

By comparing the σ-profiles of the coagulants involved in this study, the presence of choline chloride brought significant peaks in the hydrogen bond donor region, *i.e.* at around -0.9 e nm^{-2}. This peak interacts well with the peaks of paracetamol in the hydrogen bond acceptor region, *i.e.* 1.4 e nm^{-2}. In addition, the peaks of malonic acid (1.1 e nm^{-2}), levulinic acid (1.2 e nm^{-2}) and stearic acid (1.2 e nm^{-2}) on the right side of the σ-profiles indicate significant polar interactions with the polarized peak of paracetamol on the left side (1.6 e nm^{-2}). On the other hand, the coagulants that consists of stearic acid (pure stearic acid and ChCl:SA (1:2)) show an obvious peak in the non-polar region. This peak is due to the presence of linear –CH_2 carbon chains in stearic acid, while the higher peak observed in the NADES form is due to its double molar ratio. However, as seen in the σ-potential, the non-polar attractions between the coagulants and paracetamol are very small compared to that in the polar region. Thus, it can be concluded that coagulants with straight carbon chains can be used to treat paracetamol contaminated water as long as they contain strong polar moieties. In the σ-potential plots, all coagulants showed attractive interaction in the polar regions, and relatively small attractions in the non-polar region. In the hydrogen bond acceptor region, paracetamol shows high affinity towards coagulants with negative μ values at the hydrogen bond donor region. From the investigations of the three NADESs, the attraction behaviour towards paracetamol increases in the order of ChCl:SA (1:2) > ChCl:LA (1:2) > ChCl:MA (1:1). This order is consistent with the performance of turbidity removal efficiency depicted previously in Figure 5. Furthermore, when comparing this specific region with all coagulants involved, the attraction behaviour at this region increased in the order of ChCl > ChCl:SA (1:2) > ChCl:LA (1:2) > ChCl:MA (1:1) >> levulinic acid > malonic acid > stearic acid. This ranking is almost identical to our experimental turbidity removal efficiency results, where ChCl is the only coagulant that showed significant deviation. Thus, it can be assumed that the polarity of coagulants with respect to the hydrogen bond donor ability influences the efficiency of turbidity removal.

4. CONCLUSION

High turbidity removal performances were demonstrated by using NADESs in this study. In a simulated wastewater containing paracetamol, ChCl:SA yielded the highest turbidity removal performances at 97.5 %, closely followed by ChCl:LA and ChCl:MA at 97.0 and 96.4 %, respectively at its optimized operating conditions. Optimal conditions were also applied for application of the individual fatty acid constituents. Under optimal conditions, the constituent components can also work efficiently on reducing turbidity of paracetamol-contaminated wastewater at a TRE range from 87–93 %. As a result, NADESs have been demonstrated to be able to reduce the turbidity of water to a lower value, in comparison to their individual components. The proposed NADESs can be categorized as promising solvents for the removal of turbidity caused by paracetamol in water and are preferable as novel coagulants owing to the simplicity of synthesis and application. As a preliminary study in applying NADESs for turbidity removal, these novel coagulants (ChCl-DES) require further studies in effluent treatment applications.

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Prirodni duboki eutektički rastvarači za uklanjanje zamućenosti iz sintetičke farmaceutske otpadne vode

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(Naučni rad)

Izvod

Kontaminacija vodnih resursa otpadom aktivnih farmaceutskih sastojaka je među glavnim problemima životne sredine. Da bi se sprečili veliki poremećaji u prirodnim vodama, treba uspostaviti efikasan i ekološki prihvatljiv postupak uklanjanja zamućenja od strane uobičajenih zagađujućih materija, kao što je paracetamol. U ovoj studiji je istraživana upotreba nekoliko prirodnih dubokih eutektičkih rastvarača u cilju smanjivanja zamućenosti simulirane vode kontaminirane paracetamolom ispod standardne granice zamućenosti koju preporučuju Nacionalni standardi kvaliteta vode u Maleziji (50 NTU). Određeni su optimalni radni parametri (količina eutektičkih rastvarača, vreme mešanja i radna pH vrednost). Pod optimizovanim uslovima, korišćenje eutektičkog rastvarača na bazi stearinske kiseline dovelo je do najvećeg smanjenja zamućenosti od 97,5 %. Visoke performanse koagulacije su ispitivane na osnovu molekularne interakcije, korišćenjem COSMO-RS (COnductor like Screening MOdel for Real Solvents) σ-profila i σ-potencijala (histogram raspodele gustine naelektrisanja preko molekularne površine) i pokazali su visok afinitet između eutektičkih rastvarača i paracetamola. Zaključeno je da su eutektički rastvarači obećavajući kandidati za uklanjanje zamućenosti vode izazavane prisustvom paracetamola i prikladni su u daljim istraživanjima tretmana otpadnih voda.

Ključne reči: Aktivni farmaceutski sastojci; flokulacija; koagulacija; tretman otpadnih voda