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Synthesis, Characterization and Evaluation of Some Green Mannich Nano-Dispersant from Egg-Albumin

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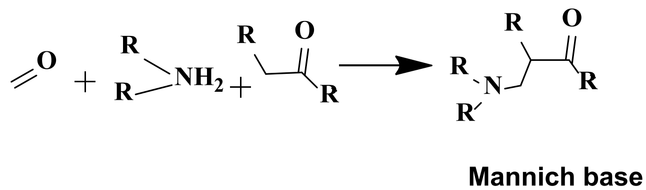
Abstract

The reaction of various aldehydes (formaldehyde, benzaldehyde, acetaldehyde and salicyaldehyde), albumin as an amine, and benzophenone as a ketone were synthesized into the four green basements of Mannich. The prepared compounds were characterized by determination of melting point and the structure was elucidated using FTIR spectrophotometer. The particle size, the zeta potential parameters and the morphological properties for the prepared compounds were characterized. The effect of the prepared compounds as oil spill dispersants for sweet water was evaluated and they have good efficiency as oil spill dispersants.

Keywords: *Mannich base; Egg – albumin; FT-IR; Zeta potential; SEM, Oil spill dispersion.*

1. Introduction

The end product of Mannich reaction is the Mannich base, beta-amino ketones containing compounds [1-4]. The Mannich reaction is a nucleophilic replacement reaction involving an amino (primary or secondary) and formaldehyde (any Aldehyde) compound condensation with active hydrogen [5]. The general Mannich reaction is represented in Scheme 1.



Scheme 1. Mannich base formation

Studies have shown Mannich bases to be highly reactive and to be convertible easily into compounds such as reduced to physiologically active amino alcohols [6]. It has been stated that Mannich bases have powerful action, such as anti-inflammatory activity [7-8], anticancer [9-10], anti-filarial activity [11]). Mannich bases are well known for their use in detergents additives [12-13], resins, polymers, surface active ingredients [14] and so on as well as in biological activity. Different active compounds have been able to solve these constraints with Mannich drugs [15]. For the synthesis of bioactive molecules, the Mannich bases and their derivatives are intermediates [16-17]. The Mannich reaction is widely used in nitrogen compound construction. Because of their use in antibacterial action [18], Mannich bases gained popularity and other applications are in agrochemical products such as plant growth regulators. In the present work four green Mannich bases were synthesized and characterized by determination of melting point, FT-IR spectrophotometer, zeta potential and the morphological structure was carried out by scanning electron microscope. The effect of the prepared compounds as oil spill dispersants was studied.

2. Materials and methods

2.1. Materials

Formaldehyde; LOBA CHEMIE 99.00%, acetaldehyde; JANSSEN CHIMICA 99.00%, benzaldehyde; LOBA CHEMIE 100%, salicyaldehyde; HIMEDIA 99.00%, benzophenone; LOBA CHEMIE 99.00% and albumin; LOBA CHEMIE 99.50% were used without further purification.

2.2. Methods

Four Mannich bases were synthesized using (2:1:2) molar ratios of aldehydes (formaldehyde, acetaldehyde, benzaldehyde and salicylaldehyde) separately, ketone (benzophenone) and amine (egg- albumin). The reaction was carried out at 70-100^{o}C, using 1 mL of concentrated hydrochloric acid as a catalyst for water removal.

2.2.1. Recrystallization process

The recrystallization process was carried out. The prepared compounds were recrystallized by heating with hot water as a solvent for recrystallization, after complete dissolving of the solute; the crystallization beaker was removed and cooled at room temperature. The beaker was then put in an ice-water bath and left to form crystals. Using vacuum filters, the crystals were collected and dried.

2.2.2. Determination of melting points for the prepared compounds

The melting points of the prepared compounds were measured using STUART SMP10.

2.2.3. Characterization of compounds prepared with FT-IR

The prepared compounds were characterized using Fourier Transformer Infra- Red Spectroscopy, Model Nicolet iS10-FTIR Spectrophotometer, KBr.

2.2.4. Zeta parameters characterization of the compounds prepared

The parameters of the prepared compounds were characterized by laser Doppler anemometry on a Malvern zeta-sizer, dynamic light scattering with a (3000 HSA, Malvern Instruments, UK) at 90°C at a scattering angle. This was done via the average particle size, size distribution and multiportion indicators. Dilution of formulated compounds suspensions with deionized water was used to obtain specimens. The average value ± standard deviation (S.D.) was stated per value for three measurements, Table 2.

2.2.5. The morphological characteristics of prepared compounds

Scanning electron microscop – QUANTA- FEG 250 was used for the microscopic characterization of the prepared compounds. The energy used for the acceleration beam was 20 KV. The magnification power (40-500µm) of all the micrograms was taken.

2.2.6. Assessment of the prepared compounds as oil spill dispersants

The prepared compounds were evaluated as oil spill dispersants for palm oil according to the following methods:

2.2.6.1. SFT Oil extraction and analysis

The determination of the efficiency index of oil spill dispersants was made in the test flask, followed by the sequence addition of oils, and finally the dispersant, with a volume of 120mL of tap-water equilibrated to the desired temperature. Subsequently, the 5 mL syringe tip attachment on the water surface instantly dispensed with 100 mL of oil. The dispersant was then distributed in the center of the slick which was fitted with a 1:25 Dispersant – to – oil relation (DOR) with a 100mL syringe tip fixture up to 4 mL. The flask was put in an orbital shaker for 10 minutes, the shaker was maintained at the desired rotating velocity at the end, and it was removed. At the end of the setting period, the first 2 ml sample was dried and removed and a 30 mL sample was taken in 50 mL cylinder to a separating funnel with 125 mL.

New 5 mL of three extracts using dichloromethane is made. The extract must then be modified to a final volume of 20 mL and transferred into a 50 mL crimp bottle with a teflon/aluminum seal. The glasses are maintained at 4±2°C (maximum 5 days) before examination. The methodology developed is accompanied by the oil standard process and the test procedures [19].

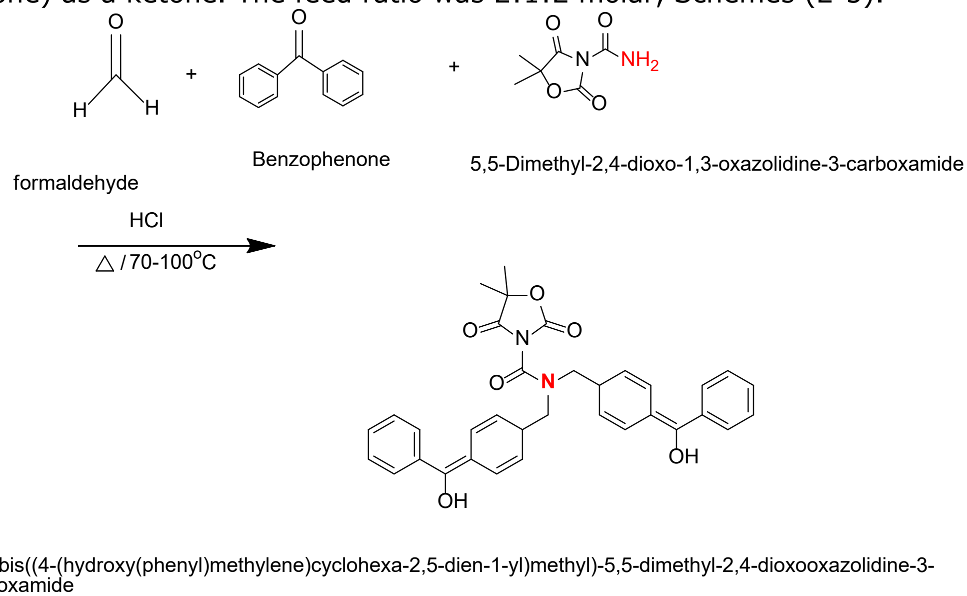
2.2.6.2. Efficiency of the prepared compounds as oil spill dispersants

The efficiency of the effect of the four prepared compounds according to (IP-AS/84) standard method at 20°C. The efficiency index (E) was calculated according to the following equation:

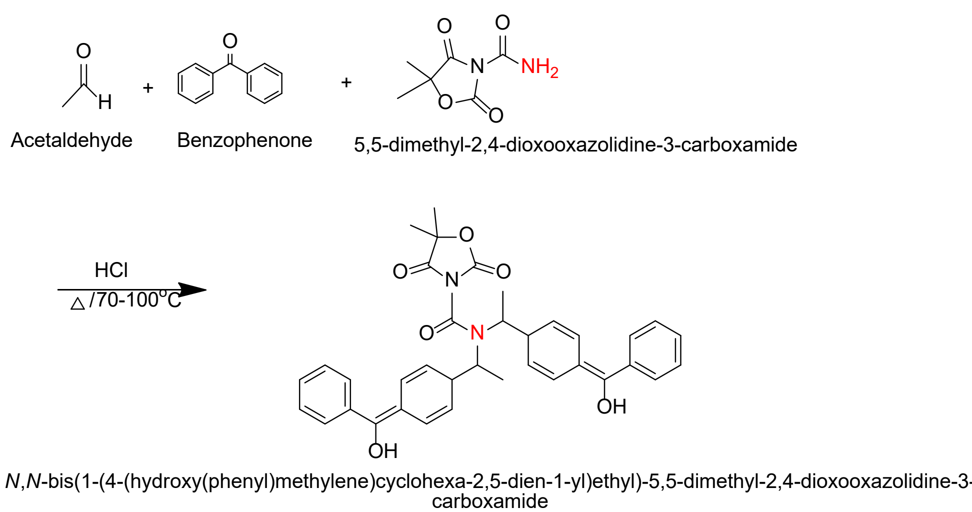
$$E = \frac{Weight\ of\ oil\ in\ 50cm3\ sample\ of\ oily\ water\ x\ 500}{Total\ weight\ of\ oil\ added\ to\ 250cm3\ \ separating\ funnel}$$

3. Results

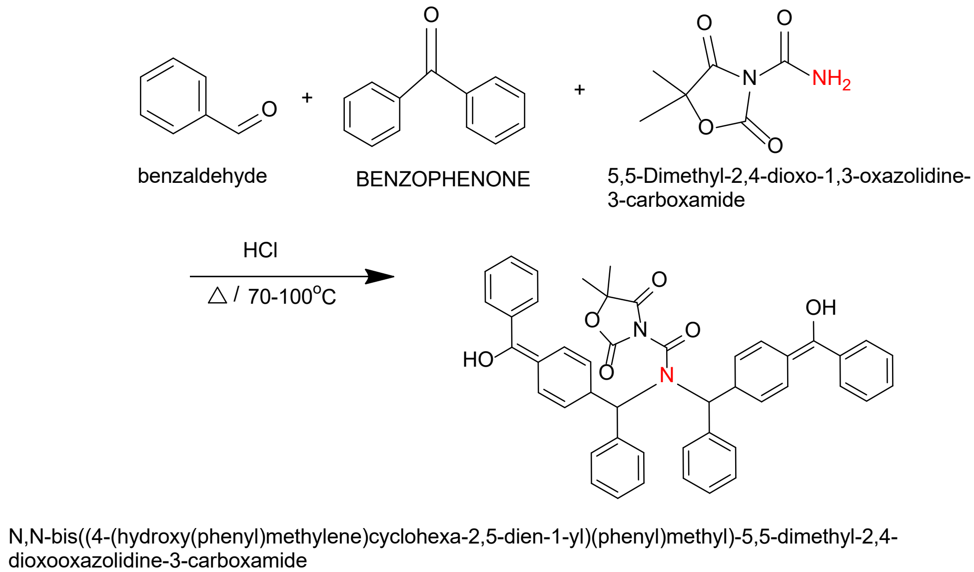
Four green Mannich bases were synthesized by reaction of different aldehydes (formaldehyde, acetaldehyde, benzaldehyde, and salicyaldehyde) separately with egg albumin and (benzophenone) as a ketone. The feed ratio was 2:1:2 molar, Schemes (2-5).



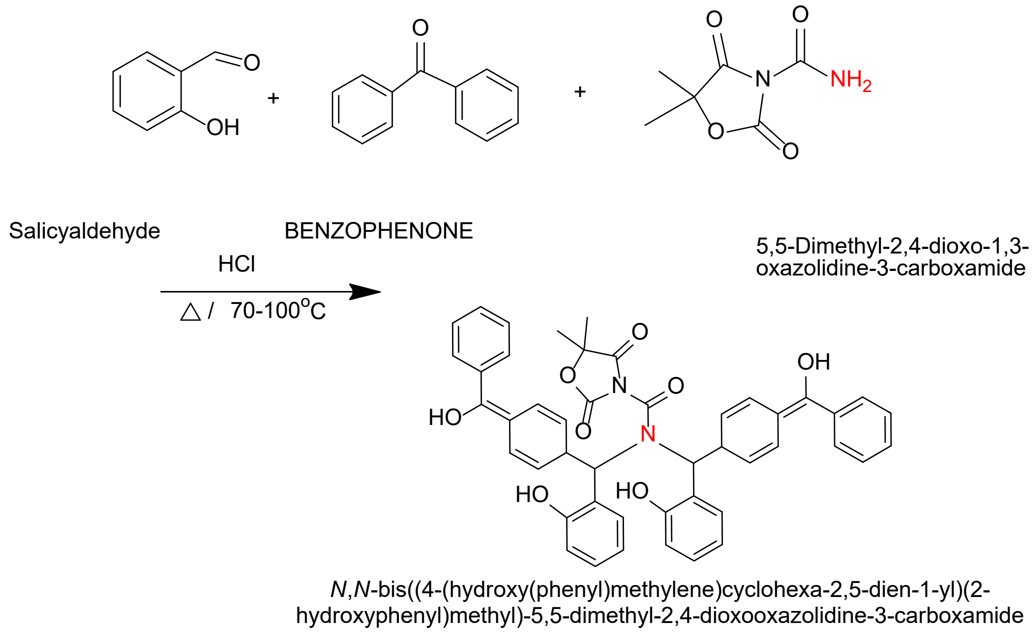
Scheme 2. A_1 Mannich base.



Scheme 3. A_2 Mannich base



Scheme 4. A_3 Mannich Base.



Scheme 5. A_4 Mannich Base.

The prepared compounds (A_1-A_4) were recrystallized and melting points were determined, data is tabulated in Table 1. The yield% of the prepared compounds was calculated according to the following equation:

$$\text{Yield \%} = \frac{actual\ yield}{theoretical\ yield} \times 100$$

The data was tabulated in Table 1. It was obvious that the A_4 compound has the greatest Yield %. This may be due to A_4 compound has the highest molecular weight of the prepared compounds.

Table 1. The designation, chemical properties of (A_1-A_4) compounds

Cpd.	Cpd. designation	M.p.(°C)	Yield %	Molecular formula	M. wt.
A_1	Formaldehyde: Albumin: benzo-phenone	146-148	92	$C_{34}H_{32}N_2O_6$	564.63
A_2	Acetaldehyde: Albumin: benzophe-none	198-200	93	$C_{36}H_{36}N_2O_6$	592.68
A_3	Benzaldehyde: Albumin: benzo-phenone	192-194	92	$C_{46}H_{40}N_2O_6$	716.82
A_4	Salicyaldehyde: Albumin: benzo-phenone	184-186	95	$C_{46}H_{40}N_2O_8$	748.82

The zeta potential parameters were determined as tabulated in Table 2.

Table 2. Zeta potential parameters of the prepared compounds

Sam-ple	Dispersant name	RI	Viscosity (cP)	DDC	Conductivity (ms/cm)	ZP (mv)	ZD (mv)	Average size - z (d. nm)	pdi
ALB.					0.209	-13.8	-13.8±4.48	401.7	0.731
A_1					0.0141	-4.39	-4.39±4.38	1386	0.895
A_2	water	1.33	0.8872	78.5	0.726	5.96	5.96±4.65	4418	0.321
A_3					0.178	8.08	8.08±3.66	2402	1.000
A_4					0.153	-0.0857	-0.0857±4.74	1870	0.384

The prepared Mannich bases were subjected to surface morphology study by scanning electron microscopy QUANTA- FEG 250, using liquid nitrogen, Figure 1.

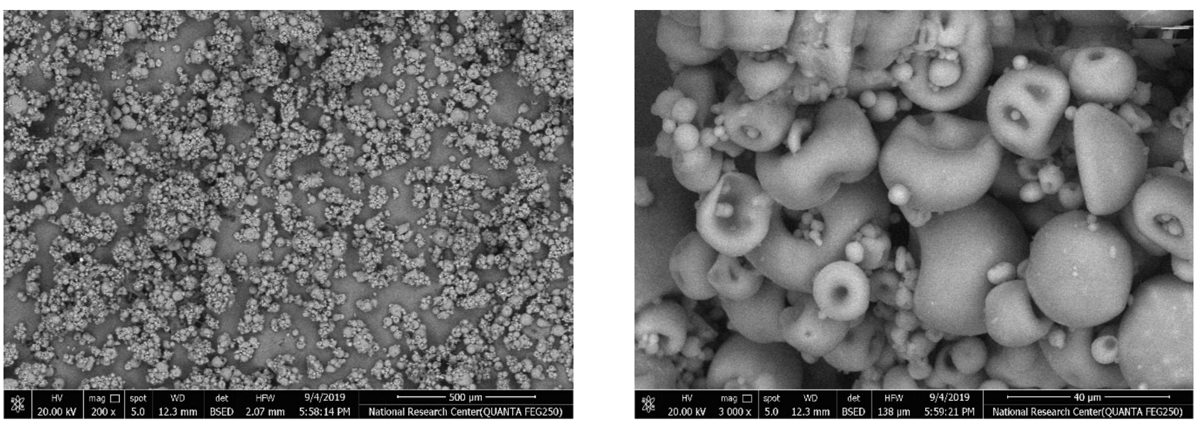


Figure 1. SEM morphology for compound A_1

4. Discussions

The chemical structure of the prepared compounds was described with FT-IR spectroscopy, from FT-IR spectra, Figure 2. By comparing FT-IR spectra of the prepared compounds with the FT-IR spectra of albumin one can concluded that the disappearance of the – NH_2 peaks at 3442 and 3360cm^{-1}. This indicate the completely conversion of – NH_2 group into tertiary amine group.

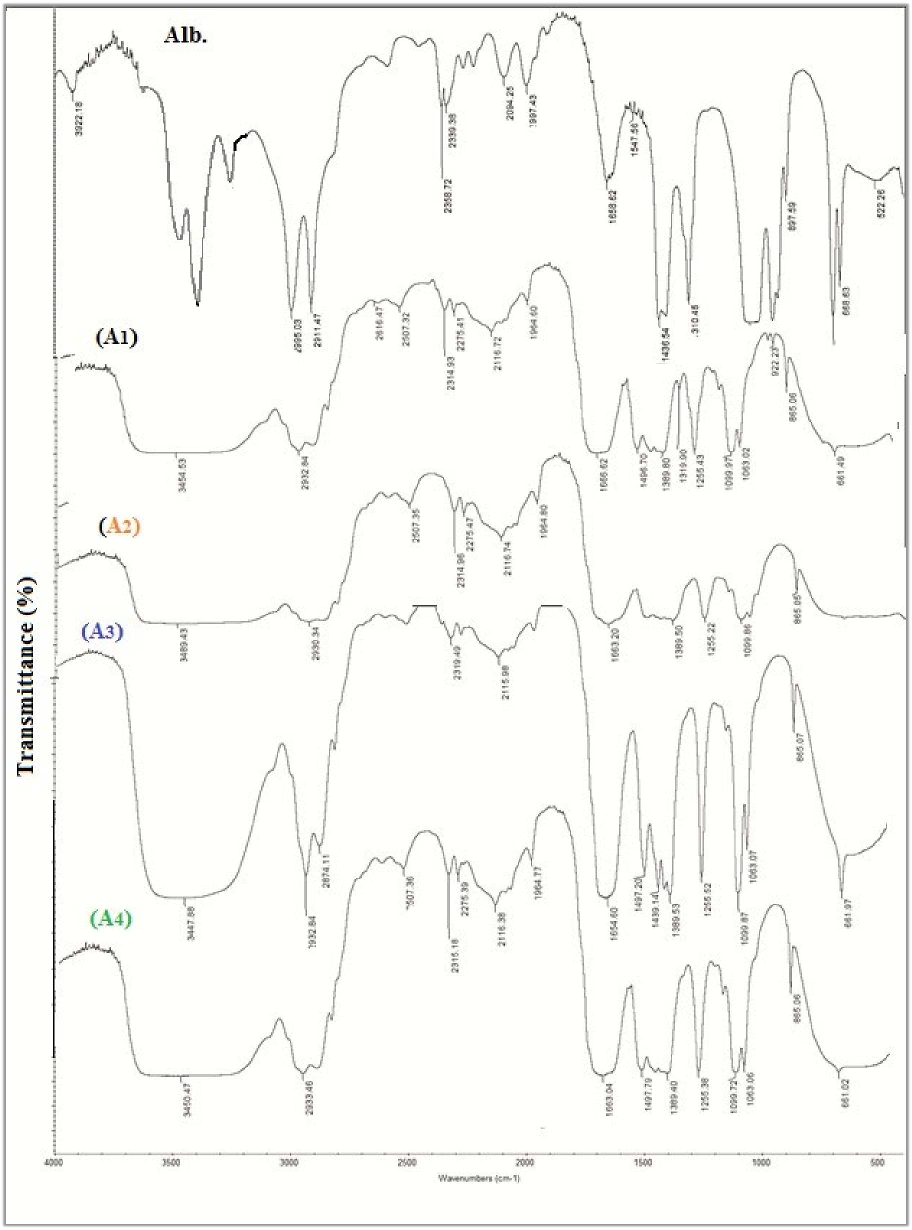


Figure 2. FT-IR of albumin and the prepared (A_1-A_4) compounds.

The specific physical and chemical properties of palm oil were characterized; the data were tabulated at Table 3.

Table 3. Physicochemical properties of palm oil

Physicochemical properties	Palm oil	SON standard
Smoke point (°C)	121	--
Flash point (°C)	182	--
Fire point (°C)	196	--
Moisture (%)	0.24	0.29
Specific gravity	0.824	0.897-0.907
Free fatty acids	3.10	3.5
Iodine value	29.56	45-53
Peroxide value	7.90	10
Saponification value	195.20	195-205

To obtain the best results the dispersant used has to be carefully selected. The effect of any dispersant depends on many factors, such as the nature of the dispersant itself, the nature of the oil spilled, and the temperature [20-21]. Thus, dispersants efficiencies on the oil were determined and given in Table 4. The results obtained show that in case of chemical dispersants (A_1-A_3), having two OH group, accordingly they have good dispersing effect ranging from (63 –74), while compound (A_4) has the highest dispersing power (88), this may be due to the presence of four OH groups besides the increase of the electron cloud inside the molecule.

Table 4. Efficiency of dispersants on oil at 20°C

Dispersant	Weight of oil in 50cm^3 sample of oily water	Total weight of oil added to 250cm^3 separating funnel	Efficiency @ 20°C
A_1	1.26	10	63
A_2	1.30		65
A_3	1.48		74
A_4	1.76		88

Different ratios were taken to determine the relation between the efficiency and DOR. As it obvious from Figure 3, it was found that the highest efficiency of the used compounds (A1-A4) according to DOR method is 1:50.

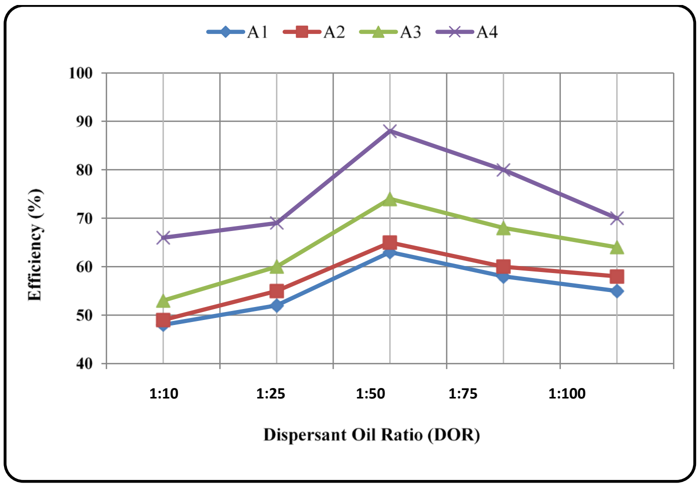


Figure 3. Efficiency of (A_1-A_4) on palm oil

5. Conclusions

In the present work four Mannich bases were synthesized and characterized by determination of melting point. The yield % of the prepared compounds was calculated and it was found that, A1 compound has the highest yield. The chemical structure of the prepared compounds was elucidated using FT-IR spectroscopy. The FT- IR spectra of the prepared compounds illustrate the disappearance of - NH_2 group of albumin and indicate the complete conversion of it into tertiary amine. Zeta parameters were characterized. The prepared compounds were evaluated as oil spill dispersants and they were obtained a good oil spill dispersant effect.

Abbreviations

FT-IR	*Fourier Transformer Infra-Red spectrophotometer;*
DOR	*dispersant oil ratio;*
SFT	*the swirling flask test*
E	*efficiency index*
RI	*refractive index*
DDC	*dispersant dielectric constant*
ZP	*Zeta potential*
ZD	*Zeta deviation*
pdi	*polydispersity index*

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Author contributions

The manuscript was written through contributions of all authors. Rabab M. Nasser, suggested the idea and contributed the writing of the paper. Asmaa G. Komier and Bushra Y. Madkhali help in the experimental part of the work.

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