LOW TOXICITY DEEP EUTECTIC SOLVENT-BASED FERROFLUID FOR THE DETERMINATION OF UV FILTERS IN ENVIRONMENTAL WATERS BY STIR BAR DISPERSIVE LIQUID MICROEXTRACTION

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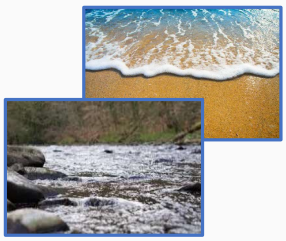
INTRODUCTION

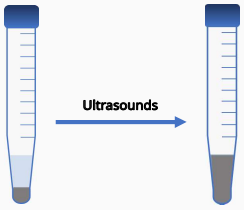
In this work, a new ferrofluid has been developed as solvent for liquid-phase microextraction techniques. The ferrofluid was composed by a menthol:thymol **low toxicity deep eutectic solvent (LT-DES)** and cobalt ferrite magnetic nanoparticles (MNPs) coated with oleic acid ($CoFe_2O_4$@OA).

This ferrofluid was employed for the determination of UV filters in environmental waters using **stir bar dispersive liquid microextraction (SBDLME)** as microextraction approach and **liquid chromatography tandem mass spectrometry (LC-MS/MS)** as measurement technique.



EXPERIMENTAL

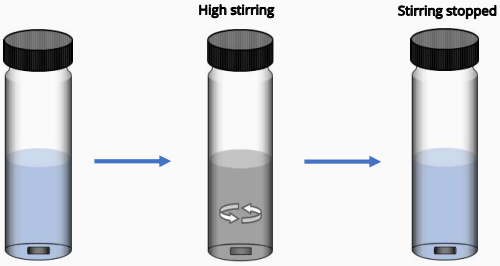
Synthesis



1 mL previously prepared LT-DES 25 mg MNPs

Ferrofluid

SBDLME



15 mL of sample 0.1 mL ferrofluid 0.2 mL ACN

Desorption and measurement

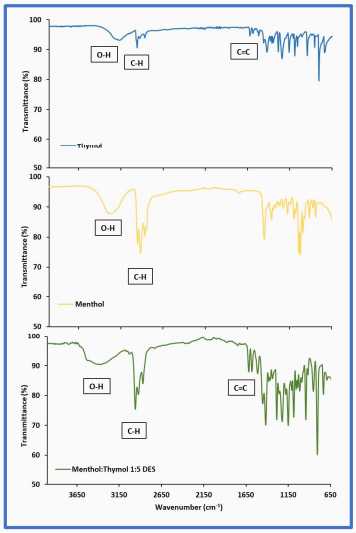
Ferrofluid 0.25 mL ACN

LC-MS/MS

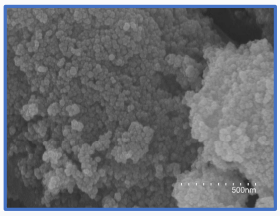
RESULTS AND DISCUSSION

Characterization

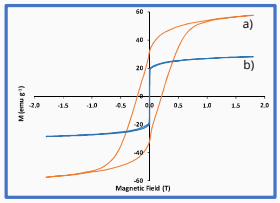
FT-IR spectra of **thymol**, **menthol**, and **menthol:thymol** LT-DES



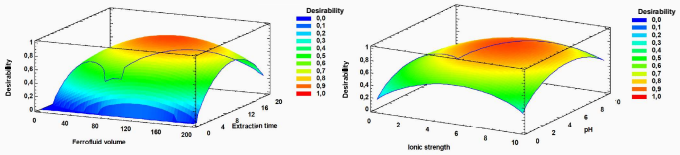
SEM image of **$CoFe_2O_4$@OA MNPs**



Magnetization curve of a) **$CoFe_2O_4$@OA MNPs** and b) **ferrofluid**



Optimization



Validation

UV filter	R^2	EF	LOD (ng L^{-1})	LOQ (ng L^{-1})	Repeatability (%RSD)						Relative recovery (%)
					Intra-day			Inter-day			
					Level 1	Level 2	Level 3	Level 1	Level 2	Level 3	
BZ3	0.9999	93	20	67	4.5	13.8	9.6	12.2	12.7	5.6	83-113
IMC	0.9998	75	16	54	6.6	6.1	5.0	9.9	12.8	14.2	80-112
MBC	0.9993	80	39	130	5.2	9.3	5.0	12.5	8.0	4.8	80-120
DHHB	0.9998	73	8	25	8.3	8.8	2.7	12.8	14.9	10.7	89-115
OC	0.9999	46	18	60	10.8	9.5	3.2	7.3	2.8	4.5	86-112
EHDP	0.9993	101	7	24	12.8	10.1	1.8	8.6	11.1	9.1	88-116
BMDM	0.9993	71	36	116	8.6	9.1	4.5	13.0	4.9	8.6	94-115
EHS	0.998	78	83	276	6.0	10.7	3.4	12.5	11.1	10.8	80-103

- **Good analytical features** were obtained for all the analytes.
- The method was applied to **three environmental waters,** finding trace amounts of the UV filters.

UV Filter	Found concentration (ng L^{-1})		
	Beach 1	Beach 2	River
BZ3	225±25	<LOQ	<LOD
IMC	<LOD	<LOD	<LOD
MBC	148±13	<LOQ	<LOD
DHHB	58±6	<LOQ	<LOQ
OC	78±9	84±7	208±2
EHDP	<LOQ	<LOQ	<LOD
BMDM	240±20	<LOQ	<LOD
EHS	<LOQ	<LOQ	<LOD

CONCLUSIONS

- A new low toxicity deep eutectic solvent (LT-DES)-based ferrofluid has been successfully prepared as an efficient extraction phase for microextraction purposes.
- Ferrofluid components are less toxic and harmful to the environment than other magnetic extraction fluids (i.e., MILs).
- Moreover, the synthesis is simpler and safer compared with other magnetic fluids (i.e., MILs), since only a water bath and an ultrasounds are needed.
- This ferrofluid was employed for the determination of UV filters in environmental waters and the proposed method showed similar results than previous methodologies, proving the potential of this ferrofluid as a cheaper and greener alternative to be employed in future analytical approaches.

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A. Duque, J. Grau, J.L. Benedé, R.M. Alonso, M.A. Campanero, A. Chisvert, Low toxicity deep eutectic solvent-based ferrofluid for the determination of UV filters in environmental waters by stir bar dispersive liquid microextraction, Talanta. 243 (2022) 123378

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Low toxicity deep eutectic solvent-based ferrofluid for the determination of UV filters in environmental waters by stir bar dispersive liquid microextraction

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ABSTRACT

In this work, a low toxicity deep eutectic solvent-based ferrofluid is presented for the first time as magnetic fluid to be used as an efficient solvent in liquid-based microextraction techniques. This ferrofluid is made of a hydrophobic deep eutectic solvent, composed by menthol and thymol in a 1:5 molar ratio as carrier solvent, and oleic acid-coated cobalt ferrite ($CoFe_2O_4$@oleic acid) magnetic nanoparticles. This material was characterized via magnetism measurement, scanning electron microscopy, infrared spectroscopy and density measurement. The determination of UV filters in environmental water samples was selected as model analytical application to test the extraction performance of this new ferrofluid by employing stir bar dispersive liquid microextraction, prior to liquid chromatography-tandem mass spectrometry analysis. The response surface methodology was used as a multivariate optimization method for extraction step. Under the optimized conditions, good analytical features were obtained, such as low limits of detection between 7 and 83 ng L^{-1}, good repeatability (relative standard deviations, RSD (%) below 15%), enrichment factors between 46 and 101 and relative recoveries between 80 and 117%, proving the good extraction capability of this ferrofluid. Finally, the method was successfully applied to three environmental waters (beach and river waters), finding trace amounts of the target UV filters. The presented low toxicity deep eutectic solvent-based ferrofluid results to be a good alternative to conventional solvents used in liquid-phase microextraction techniques.

Ver Publicación

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