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Nonionic Microemulsion Extraction of Ni (II) from Wastewater

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Two W/O microemulsion systems, Water/iso-C3-ol/Brij 30/PO and Water/Brij 30/EtOAc, have been proved to have high yields in removal and recovery of metal ions (Ni (II)) from wastewater. The influence of some parameters, such as aqueous phases to microemulsion volumetric ratio, oil type, concentration of the surfactant and distribution coefficient of Ni (II) between aqueous and microemulsion phases, on separation of nickel ion from aqueous solution have been studied. The extraction of Ni (II) is very efficient for concentrations of nickel aqueous solutions less than 1000 mg/L, when the extraction efficiency is up to 85%.

Keywords Distribution coefficient; nickel extraction; non-ionic microemulsion

Introduction

Nanotechnologies hold great promise for reducing the production of wastes, decreasing industrial contamination, developing efficient systems for removal, recovery and recycling of different pollutants from wastewater and improving the efficiency of energy production and use. An efficient wastewater treatment process is assured by high yield extraction of pollutants and its ability for recycling or degradation to a non-effect dose. One way to achieve this goal is based on microemulsion extraction, recovery and recycle or decomposition of pollutants from wastewater. Microemulsion is an effective and environmental – friendly method for metals removal based on nanostructured systems as nonconventional process of liquid – liquid extraction.

A microemulsion is defined as a system formed by the dispersion of nanodroplets of two immiscible liquids, stabilized by an interfacial membrane formed by surfactant and cosurfactant. They are thermodynamically stable, homogeneous and optically isotropic solutions. In excess of oil, the microemulsion coexists with an

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oil continuous phase (Winsor I) and in excess of water it coexists with an aqueous continuous phase (Winsor II). In Winsor III system three phases are present, where the microemulsion is in equilibrium with both excess aqueous and organic phases and in Winsor IV only one microemulsion phase is formed [1,2].

Among the hazardous wastes, metals have attracted attention for their removal from industrial effluents and developing various wastewater treatment methods [3–7]. The ability of microemulsion to form phases with different polarities, acidities and viscosities where solutes of very different structure can be solubilized has promoted its use for metallic ions extraction from wastewater [3,5,8] followed by their recycling as nanoparticles [9]. This method offers several advantages such as enhanced selectivity, no need of processing at high temperature or pressure, cost effective and less time consuming.

In this respect, the aim of this work is the application of microemulsion systems containing an oil component (Ethyl Acetate (EtOAc), Pinus Oil (PO)) and a nonionic surfactant (Brij 30) to removal and recovery of metal cations (Ni (II)) from wastewater. While in case of anionic surfactants the effect of pH on their solubilization and on the microemulsion type can not be neglected, the situation is no longer the same when nonionic surfactants are considered. The low toxicity of the two oils and their limited persistence in environment are important advantages for their use in pollutants extraction. In addition, PO has a low corrosion level and a limited persistence, while EtOAc is a low cost oil. Specific physico-chemical parameters known to have significant influence on the existence domain of the microemulsion within phase diagram have been investigated (water/oil ratio, nature of oil, concentration of surfactant) in order to determine their effect on the separation of nickel ion from aqueous solution and to find out the proper microemulsion extraction system. The distribution coefficient has been also determined in order to select the optimum volumetric ratio of aqueous phase to microemulsion.

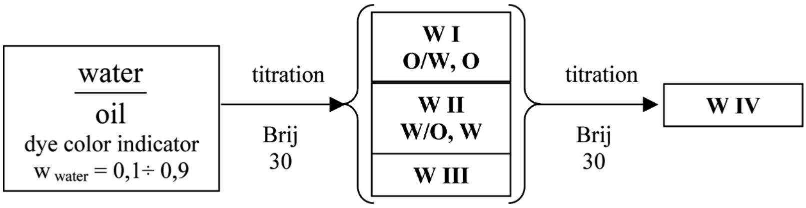
Methodology

Materials

Pinus Oil (PO) was obtained from FARES BIO VITAL Laboratories, Romania. Polyoxyethylene-4-lauryl ether (Brij 30), Ethyl Acetate (EtOAc), and Isopropyl Alcohol (iso-C3-ol) were purchased from SIGMA ALDRICH and Nickel (II)-Nitrat-Hexahydrat from MERCK. All materials were used as received. Ultra-pure water (Millipore Corporation) was used.

Construction of Phase Diagram

In order to find out the region where microemulsion can be formed, ternary and pseudo-ternary phase diagrams were built using surfactant titration method at ambient temperature (298 ± 1 K). Oil/water immiscible mixtures were titrated with surfactant in certain proportion until the two clear transparent phases, microemulsion (W/O or O/W) and phase in excess, (W or O, respectively) were separated, and the mass of surfactant was registered. The titration with surfactant was continued until the two mixtures have been turned into a clear transparent one phase, and the mass of surfactant was registered again. The phase transition was detected by using a dye colour indicator (Scheme 1).



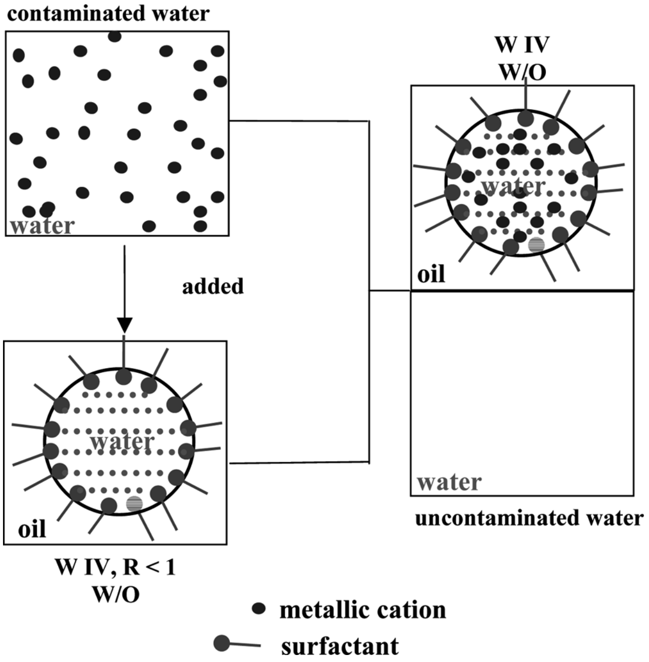
Scheme 1. Construction of phase diagram.

Extraction Process

During extraction process, the W/O microemulsion phase was placed in contact with a Ni (II) aqueous solution and stirred until the Ni (II) distribution equilibrium was achieved. Then the occurrence of complete two phase separation, microemulsion – rich in metal and aqueous phase in excess – poor in metal, was obtained (Scheme 2).

In all studies performed the temperature was maintained at 298 ± 1 K, and the nickel concentrations were ranging between 25 mg/L and 2500 mg/L. The influence of volume ratio of aqueous phase to microemulsion, expressed as *F*, on the extraction yield was investigated in the range of 1 to 5.

Nickel extraction yields were calculated after separation of the two phases. After extraction, the nickel concentrations in aqueous phase were measured by atomic absorption spectrometry (Analytik Jena AAS-6Vario) while the nickel content in microemulsion phase was calculated by mass balance.



Scheme 2. The extraction process based on surfactant aggregation in the oil phase.

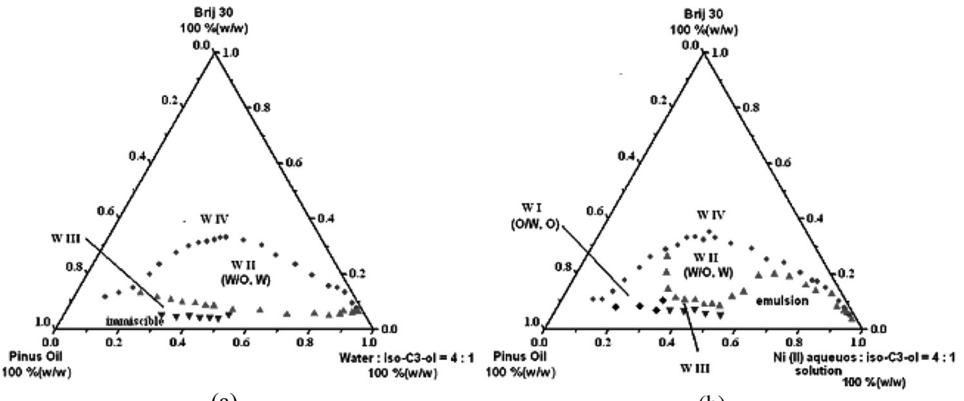
Results and Discussion

Phase Diagrams in the Ternary System Water/Brij 30/Ehtyl Acetate and in Pseudo Ternary System Water/ Isopropyl Alcohol /Brij 30/Pinus Oil

Prior the extraction the phase diagrams have been drawn in ternary and pseudo – ternary systems water – Brij 30 – Oil. Then these diagrams were used to select the optimum system and composition domain for conducting extraction of heavy metals (Ni (II)) from aqueous media (Figs. 1 and 2).

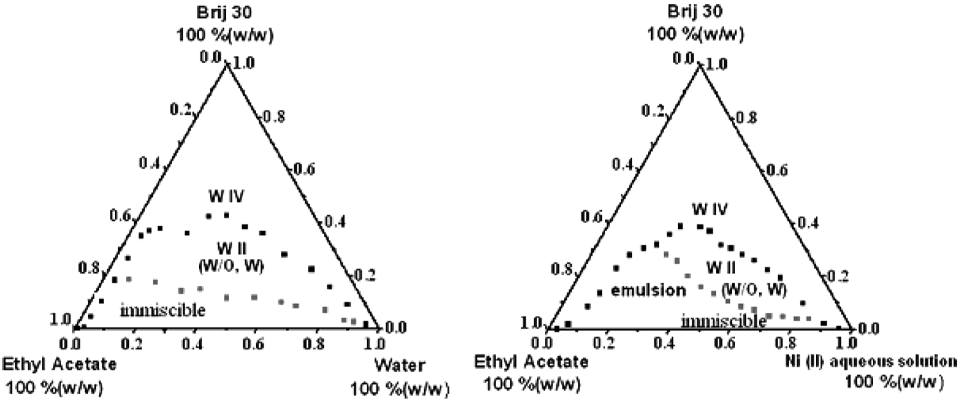
Studies of the phase transitions of these systems showed that W/O microemulsions are easily formed. The short-chain alcohol, iso-C3-ol, is used to obtain the desired phases. However, due to its miscibility with water, iso-C3-ol acts as a co-solvent and tunes the curvature by changing the polarity of the solvent and not by changing the surfactant direct packing towards phase inversion (Fig. 2).

When the iso-C3-ol is used as cosolvent, the Winsor II (W/O, W) region is extended enough to be able to extract metallic cations from water, for a given water/alcohol ratio, r = 4. The Winsor II (W/O, W) regions are delimited by Brij 30 over a large concentration range (5 to 40% (w/w). By using EtOAc oil, the Winsor II area is larger than that corresponding to Water/iso-C3-ol/Brij 30/PO system due to their different chemical nature and miscibility. The EtOAc is an ester oil, partially water soluble, while PO consists mainly in cyclic terpene alcohols, which are water insoluble [10]. The partial water/EtOAc miscibility occurs by the transfer of the EtOAc molecules from the interface into aqueous phase, resulting in the destabilization of the repulsive forces between surfactant polar heads. Similar effect of iso-propanol as cosolvent on phase transitions within Water/Brij 30/PO system could be also noticed. Moreover, the addition of Ni (II) into Water/iso-C3-ol/Brij 30/PO system produced the reduction of the contaminated water/microemulsion volumetric ratio, F, from 10 to 1 (Fig. 1b), while, the Water/Brij 30/EtOAc system is able to decontaminate water volumes corresponding to F ranging between 1 and 5 (Fig. 1a). The reason for this might be the decrease of interfacial tension, as a consequence of accumulation of surfactant molecules and Ni (II) cations at the interface resulting into the hydrophilic nanodroplet core. These nanodroplets are used to



(a) (b)

Figure 1. The phase diagrams at 298 K for Water/iso-C3-ol/Brij 30/PO (a) and Ni (II) aqueous solution/iso-C3-ol/Brij 30/PO (b) systems; 1 phase: direct or reverse micelles, Winsor IV system, gel or liquid crystals; 2 phases: Winsor II system (W/O, W).



(a) (b)

Figure 2. The phase diagrams at 298 K for Water/Brij 30/EtOAc (a) and Ni (II) aqueous solution/Brij 30/EtOAc (b) systems; 1 phase: direct or reverse micelles, Winsor IV system, gel or liquid crystals; 2 phases: Winsor II system (W/O, W).

transport metal ions from the aqueous phase to the organic phase which normally lead to increased extraction yields (Figs. 3–7).

The Effect of Surfactant Concentration (Brij 30) on Extraction Yield

The concentration of surfactant is related to the initial microemulsion phase, it does not include the wastewater volume. The increase of the surfactant concentration (Brij 30) results in quite high extraction yields for both systems (Figs. 3 and 4).

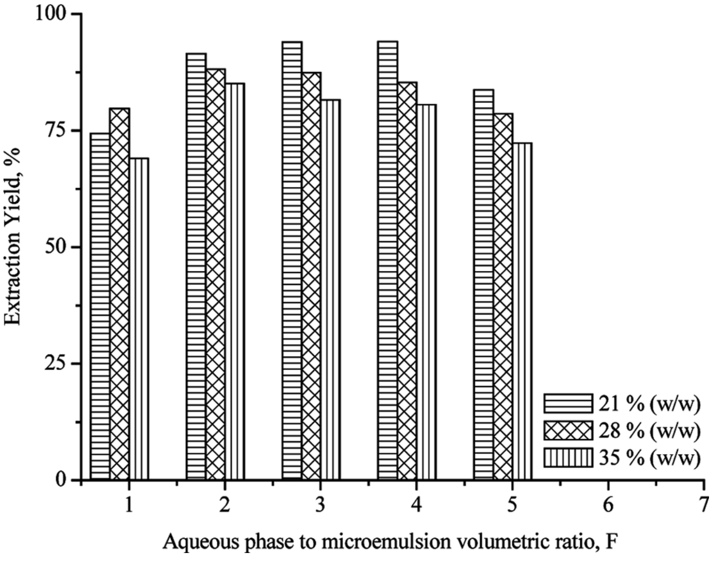


Figure 3. The surfactant concentration effect on the extraction yield of Ni (II) from aqueous solution by Water/Brij 30/EtOAc system.

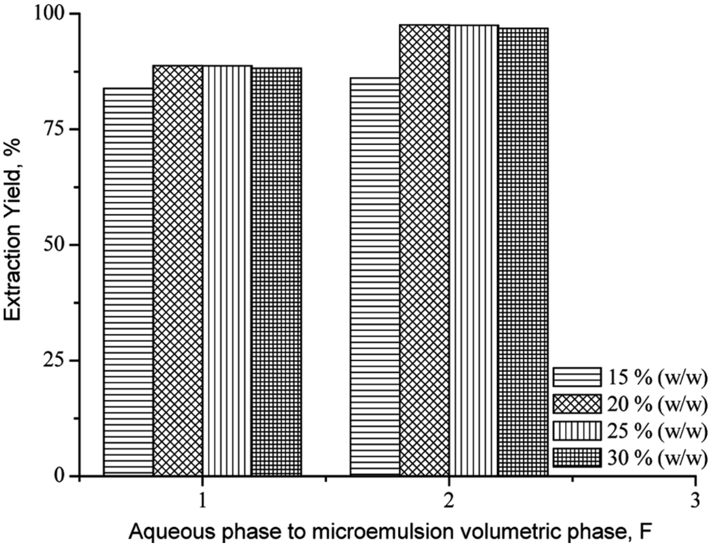


Figure 4. The surfactant concentration effect on the extraction yield of Ni (II) from aqueous solution by Water/iso-C3-ol/Brij 30/PO system.

It can be noted that the optimum surfactant concentration for Ni (II) extraction from wastewater is around 21% (w/w) for both systems tested. The use of higher surfactant concentrations for extraction by Water/iso-C3-ol/Brij 30/PO system is not economically justified even the extraction yield is slightly increased.

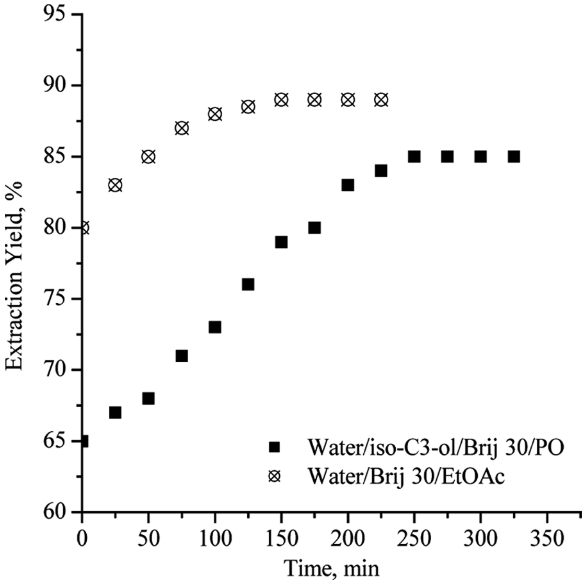


Figure 5. The contact time effect on the extraction yield of Nig (II) from aqueous solution by Water/iso-C3-ol/Brij 30/PO and Water/Brij 30/EtOAc systems, at 21% (w/w) Brij 30 and F = 2.

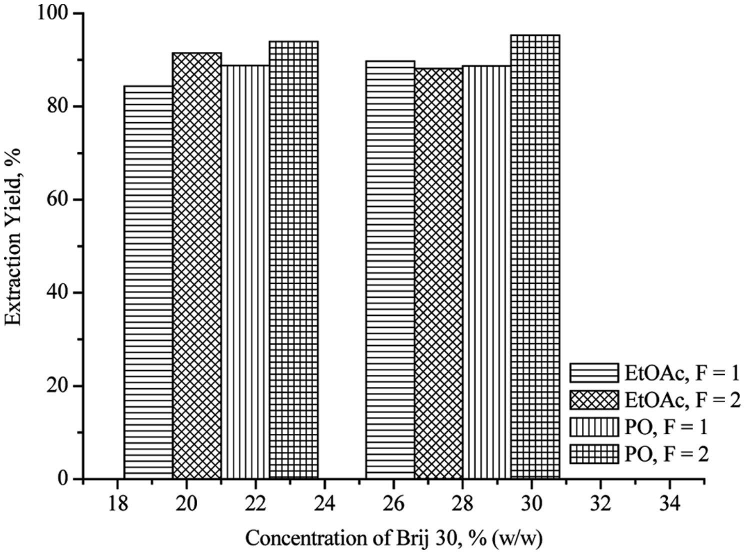


Figure 6. The effect of oil type on Ni (II) extraction yield.

The Effect of Aqueous Phase/Microemulsion Ratio (F) on Extraction Yield

The increase of aqueous phase volume at constant surfactant concentration (21%) initially results in increased extraction yields followed by a decreasing tendency (Figs. 3 and 4). Both systems exhibit a maximum extraction yield for F = 2. Superior extraction yields were also obtained in case of Water/Brij 30/EtOAc system by contacting higher volumes of wastewater, corresponding to F = 3 and 4. These

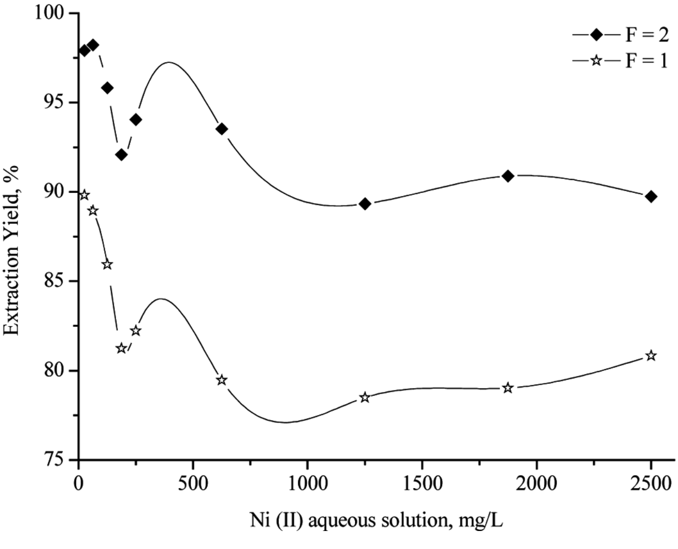


Figure 7. Nickel ion concentration effect on the extraction equilibrium of Water/iso-C3-ol/Brij 30/PO system, at 21% (w/w) Brij 30 and F = 2.

results can be explained if one considers that the hydration of oxiethylenic groups of surfactant molecules determine the increase of negative charge on the oxygen atom of water dipoles. This effect enhances the stability of the $[Ni(H_2O)_6]^{2-}$ into the hydrophilic nanodroplets core.

The Effect of Contact Time on Extraction Yield

The extraction of Ni (II) from aqueous solution to microemulsion phase has reached equilibrium within 120 min for Water/iso-C3-ol/Brij 30/PO system and 240 min for Water/Brij 30/EtOAc system (Fig. 5), resulting in high extraction yields (up to 85%).

The Effect of Oil Type on Ni (II) Extraction

The effect of these two volatile oils, EtOAc and PO, on the nickel extraction yield was further studied. The results, illustrated in Figures 5 and 6, show similar nickel extraction yields. However, a different contact time was necessary for achieving the extraction equilibrium, 2 h when using Water/iso-C3-ol/Brij 30/PO and 3 h for Water/Brij 30/EtOAc (Fig. 5).

Distribution Coefficient of Ni (II) Between Aqueous and Microemulsion Phases

The phase separation and extraction efficiency is strongly dependent on the Ni (II) ion concentration (Figs. 1, 2, and 7) as the W/O droplets become larger and more closely spaced, thus facilitating the exchange of nickel ions among droplets and between droplets and exceeding aqueous phase corresponding to Winsor II microemulsion system.

The extraction of Ni (II) is very efficient for a wide concentration range (less than 1000 mg/L) for both systems.

The nickel extraction from aqueous phase by microemulsion depends on the thermodynamic equilibrium partition of this heavy metal between the two liquid

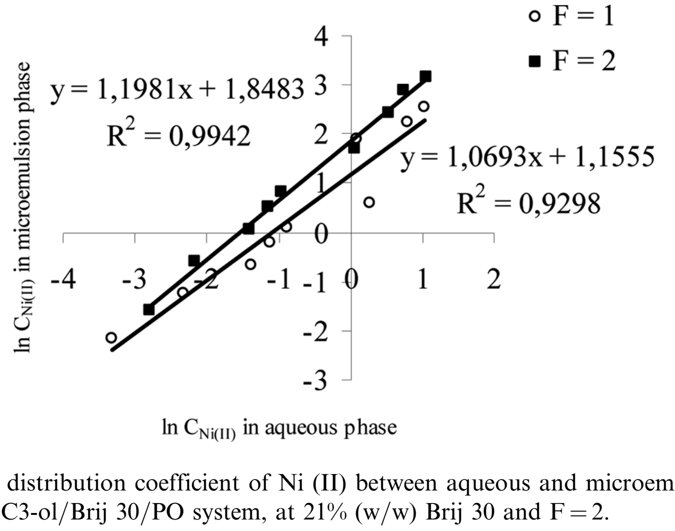


Figure 8. The distribution coefficient of Ni (II) between aqueous and microemulsion phases by Water/iso-C3-ol/Brij 30/PO system, at 21% (w/w) Brij 30 and F = 2.

phases. Assuming that, microemulsion extraction involves the distribution of Ni (II) between aqueous and microemulsion phases and the separation equilibrium is similar to that of a liquid – liquid extraction process, the distribution coefficient, D, was calculated using the Eq. (1) [11] (Fig. 8):

$$D = \frac{C_{Ni(II),\text{microemulsion}}}{C_{Ni(II),\text{aqueousphase}}} \qquad [1]$$

The results obtained on the extraction yields are in agreement with the distribution coefficients, 6.35 and 3.18 for Water/iso-C3-ol/Brij 30/PO and Water/Brij 30/EtOAc, respectively.

Conclusions

The two systems studied, Water/iso-C3-ol/Brij 30/PO and Water/Brij 30/EtOAc are able to form Winsor II system (W/O, W) which can be used for metal ions extraction. These two-phase regions are delimited by the Brij 30 concentrations ranging between 7 and 40% (w/w) and correspond to F values (aqueous phase/microemulsion volumetric ratio) up to 5. When iso-C3-ol is used as cosolvent, the Winsor II (W/O, W) region is extended.

The extraction of Ni (II) from aqueous solution to microemulsion phase has reached the equilibrium within 120 min and 240 min for Water/iso-C3-ol/Brij 30/PO and Water/Brij 30/EtOAc respectively, resulting in high extraction yields (up to 85%).

The optimum surfactant concentration is around 21% (w/w) for both systems and for F = 2 the maximum extraction efficiency is achieved in Ni (II) aqueous solution of concentration up to 1000 mg/L.

The findings of this study suggest that microemulsion systems have high applicative potential in extraction, recovery and recycle of pollutants from wastewaters.

Acknowledgments

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References

[1] Mihaly, M., Lacatusu, I., Enesca, I. A., & Meghea, A. (2008). *Mol. Cryst. Liq. Cryst.*, *483*, 228.
[2] Mihaly, M., Lacatusu, I., Enesca, I. A., & Meghea, A. (2008). *Mol. Cryst. Liq. Cryst.*, *483*, 205.
[3] Singh, A. & Turner, A. (2009). *Env. Pol.*, *157*, 646.
[4] Zhao, Y. Y., Thao, Z., Chuan-Bo, X., Xue-Mei, X., Ling, L., & Zhan-Yu, L. (2008). *Sep. Purif. Tech.*, *60*, 174.
[5] Ghezzi, L., Robinson, B. M., Secco, F., Tiné, M. R., & Venturini, M. (2008). *Coll. Surf. A.: Phys. Eng. Asp.*, *329*, 12.

[6] Ghezzi, L., Monteleone, G., Robinson, B., Secco, F., Tiné, M. R., & Venturini, M. (2008). *Coll. Surf. A.: Phys. Eng. Asp.*, *317*, 717.

[7] Dantas, T. N. C., Oliveira, K. R., Neto, A. A. D., & Moura, M. C. P. A. (2009). *Wat. Res.*, *43*, 1464.

[8] Neto, A. A. D., Dantas, T. N. C., & Moura, M. C. P. A. (2004). *J. Haz. Mat.*, *B114*, 115.

[9] Destée, C. & Nagy, J. B. (2006). *Adv. Col. Int. Sci.*, *123–126*, 353.

[10] Iovu, M. (2008). Organic Chemistry. *The Official Gazette of Romania*, RO.

[11] Vasiliu, C., Mihaly, M., & Pincovschi, I. (2005). *Sci. Tech. Env. Prot.*, *12*, 103.