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Acetaminophen extraction by emulsion liquid membrane using Aliquat 336 as extractant

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ABSTRACT

In this work, extraction of acetaminophen (ACTP), currently named as paracetamol, from aqueous solutions by emulsion liquid membrane (ELM) using Aliquat 336 as carrier was investigated. An ELM system is made up of hexane as diluent, Span 80 as the surfactant and potassium chloride as the inner aqueous solution. Influence of operating conditions that affects the permeation of ACTP such as surfactant concentration, extractant concentration, emulsification time, sulfuric acid concentration in external phase, acid type in external phase, internal phase concentration, type of internal phase, stirring speed, volume ratio of internal phase to membrane phase, treatment ratio, ACTP initial concentration and diluent type was examined. Additionally, the effect of KCl concentration in the internal aqueous phase on the stripping of ACTP and the reuse of the recovered membrane was studied. Under most favorable conditions, it was possible to extract practically all of ACTP molecules from the feed external solution. The recovery of the membrane phase was total and the extraction of ACTP was not decreased. The ELM treatment represents a very interesting advanced separation process for the removal of ACTP even from complex matrices such as natural water, sea water and sewage water effluent.

1. Introduction

In recent decades, the presence of pharmaceuticals has been documented and reported as an emerging environmental issue [1–4]. Pharmaceutical compounds have raised more attention due to the unknown environmental impact, possible damages to the botany and fauna present in aquatic systems and human health effects due to long-term exposure. The major sources of pharmaceuticals are the continuous disposal of wastewaters released from the pharmaceutical industries and excretory products of medically treated humans and animals [5]. Pharmaceutical compounds that need special attention include analgesic, antibiotics, disinfectants, hormones, cytostatic agents and immunosuppressive drugs [6]. The pharmaceutical residues have been identified and quantified in sewage treatment plant effluents, surface waters, ground water and drinking water [7].

Acetaminophen (ACTP), usually named as paracetamol, is a common analgesic and anti-inflammatory that is widely used for humans and animals. ACTP, which can be purchased in most countries even without medical prescription, is the main active ingredient of widely used analgesic and antipyretic drugs, especially as an effective substitute for aspirin for patients who are sensitive to aspirin, and safe up to therapeutic doses. ACTP toxicity is the foremost cause of severe and sometimes fatal hepatotoxicity and nephrotoxicity, which in some cases is associated with renal failure or may lead to death [8]. During therapeutic use, 58–68% of ACTP was excreted from the body unaltered [9] and it has been detected with concentrations in the range of 6–65 ppb [2,10,11] in sewage treatment plant effluent, surface water, rivers, drinking water and groundwater.

Most frequently, conventional treatment processes applied to wastewater treatment plants fail to completely remove pharmaceutical compounds. Therefore, the integration of conventional wastewater treatments with advanced technologies has become of great interest. From this point of view, emulsion liquid membrane (ELM) has gained much attention as an advanced extraction process for the removal of contaminants present in wastewater. Compared to conventional processes, ELM techniques have some attractive features, for example, simple operation, high efficiency, extraction and stripping in one stage, larger interfacial area, scope of continuous operation.

The ELM process is carried out by combining extraction and stripping steps in one stage, which leads to simultaneous purification and concentration of the solute. Separation is achieved by permeation of solute through this liquid phase from a feed phase

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to a receiving phase. The feed and receiving phases are normally miscible while the membrane phase is immiscible in both. An ELM can be considered as a double emulsion consisting of three phases: the external, membrane and internal phases. Receiving phase is emulsified in an immiscible liquid membrane with the use of surfactants and high-speed agitation. Emulsion droplets range from 1 to 3 μm in diameter, thus providing good stability [12]. The water-in-oil (W/O) emulsion, or liquid membrane, is then dispersed in the feed solution (a second aqueous phase) with constant agitation and mass transfer from the feed to the internal receiving phase takes place. Once dispersed in the continuous phase, globules of the emulsion of a diameter of 100–2000 μm form [12]. Hence, the liquid membrane serves a dual purpose of permitting selective transfer of one or more components through it from external phase to internal droplets and vice versa and preventing mixing of external and internal phases. The solute mass transfer is driven by the concentration difference between the external feed phase and the internal phase. After the desired separation, the emulsion and the continuous phase are separated in a settling step. The final step in the ELM process involves breaking the emulsion, whereby the internal phase is then recovered and the membrane phase can be reused.

To the best of our knowledge, data on the removal of ACTP from contaminated water by ELM have not been reported previously. Additionally, it is of considerable practical interest to examine the removal of ACTP in complex matrices such as natural water, sea water and sewage water effluent. Thus, this study was focused on the development of an ELM process for the extraction of ACTP from aqueous solutions. The effect of experimental conditions such as surfactant and extractant concentrations, emulsification time, sulfuric acid concentration in external phase, acid type in external phase, internal phase concentration, type of internal phase, stirring speed, volume ratio of internal phase to membrane phase, treatment ratio, diluent type and ACTP initial concentration on the extraction of ACTP by ELM was examined. Additionally, permeation of ACTP by ELM in pure water, natural water, sea water and sewage water effluent was compared. The influence of internal phase concentration on the stripping of ACT was evaluated. Additionally, the reuse of the recovered membrane was studied.

2. Materials and methods

ACTP ($C_8H_9NO_2$) stock solutions were prepared by dissolving analytical grade ACTP, purchased from Sigma–Adlrich, in distilled water. Feed solutions were prepared by addition of an acid solution into aqueous solution containing appropriate amount of ACTP. ACTP feed solutions from a known amount of ACTP stock solution were diluted with distilled water to a given concentration.

All other chemicals used in this work were of analytical grade and were purchased from Sigma–Aldrich.

The extraction of ACTP using emulsion liquid membrane involves three steps namely preparation of liquid membrane emulsion, extraction of the solute from feed by contacting the emulsion and separation of liquid emulsion from the external phase by settling.

Internal aqueous standard solutions were prepared by taking the required amount of chloride salt solution (KCl, NaCl or $CaCl_2$) in distilled water. The organic membrane phase was prepared by dissolving the appropriate amount of Span 80 as a surfactant in hexane under a gentle mixing by a magnetic stirrer. The W/O emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using a high-speed disperser (Ultra-Turrax IKA T18) for a fixed mixing time. The volume ratio of internal aqueous phase to organic phase was changed from 1/2 to 2/1.

A volume of the prepared W/O emulsion was added to 250 mL of external aqueous solution (ACTP) in a cylindrical thermostated vessel that was attached to an overhead mechanical stirrer at 250 rpm (except when the effect of stirring speed was studied). The agitator used was a 45° pitch four blades down pumping impeller (diameter 5 cm). The content of the vessel was stirred in order to disperse the W/O emulsion in the external phase at variable speeds for different contact times to make the W/O/W double emulsions. The external phase solution was periodically sampled at various time intervals. The concentration of pollutant in the solutions was determined by a UV–visible spectrophotometer set at the wavelength corresponding to maximum absorbance of the studied pollutant. Each experiment was repeated at least two times in order to verify the reproducibility. The maximum standard deviation was 2%.

Extraction efficiency was calculated using the following equation:

$$\text{Extraction efficiency } (\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 is the initial concentration of pollutant in the external phase (mg/L) and C is the concentration of pollutant in the external phase at any time (mg/L).

3. Results and discussion

The transport mechanism of ACTP by ELM using Aliquat 336 (tricaprylmethylammonium chloride) as carrier is shown in Fig. 1. The pK_a of acetaminophen is 9.50. When the pH was kept low, ACTP is present in neutral protonated form. Aliquat 336 is a cationic extractant and, therefore, acetaminophen is transferred in its anionic state by a driving force resulting from the gradient of other anionic counter-ions between the two aqueous phases. Aliquat 336 can be produced third phase formation (or a second organic phase) in systems using aliphatic diluents. Nevertheless, in the present study, this formation was not observed. In during the extraction process, the chemical reactions occurring on the feed and stripping solution side of emulsion liquid membrane (ELM) are given below:

Feed-membrane side reaction:

$$(R_3CH_3N^+Cl^-)_{org} + (C_8H_9NO_2)_{aq} \leftrightarrow (R_3CH_3N^+C_8H_8NO_2)_{org} + (H^+Cl^-)_{aq} \tag{2}$$

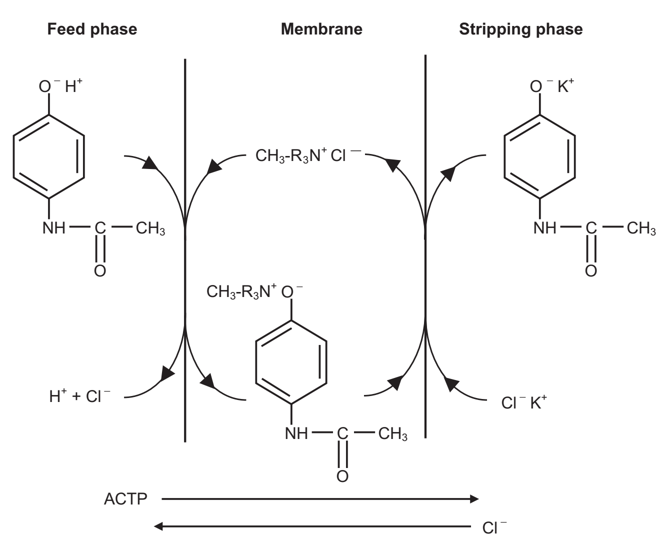

Fig. 1. Extraction mechanism of ACTP by ELM using Aliquat 336 as extractant.