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Removal of tributyl phosphate from aqueous stream in a pilot scale combined air-lift mixer-settler unit: Process intensification studies

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ABSTRACT

This work reports the removal of tributyl phosphate (TBP) from aqueous stream using organic solvent in an industrial scale combined air-lift mixer-settler unit (CAL-MSU) having 10 stages. The solute i.e., TBP is transferred from aqueous continuous (0.3 M HNO_3 saturated with TBP) to organic dispersed phase i.e., normal paraffin hydrocarbon (NPH). Effect of phase flow ratios on steady state, number of stages as well as mass transfer coefficient on TBP removal and mass transfer coefficient, is observed. The maximum TBP extraction efficiency of about 96% (201 ppm to 8 ppm) and maximum overall volumetric mass transfer coefficient of $13.3 \times 10^{-5}\,s^{-1}$ was observed at continuous phase flowrate 36 LPH and dispersed phase flowrate 24 LPH. For optimized operating parameters, the energy input per unit volume for 10-stage CAL-MSU and similar configuration 10-stage pump-mix mixer-settler are found to be 37.0 kJ/m^3 and 77.7 kJ/m^3, respectively.

1. Introduction

A wide range of equipment's is available for liquid–liquid extraction which includes columns (spray, packed, pulsed, and rotary agitated), mixer-settlers and centrifugal extractors [1,2]. Among all these type of equipments, mixer-settlers are widely used in different industries because they give a stable operation and high stage efficiency [3]. Mixer-settlers (with or without mechanical agitation) are usually preferred over pulsed column and centrifugal extractors because of longer residence time and limited head-room space [4].

As nuclear industry operates in highly radioactive and corrosive environment, in addition to physical properties of fluids and operating conditions; ease of maintenance and remote operation are two main factors which have to be considered while designing the extraction equipment. The air-agitated mixer-settlers have been used in the atomic energy establishments for many mass transfer operations in nuclear waste water stream. Air agitation offers certain advantages such as low maintenance and no sealing problem due to the absence of moving parts. However, liquids to be contacted should have low vapor pressure at the operating temperature to avoid the loss of phases with outgoing inert gas [5].

Various researchers have studied the hydrodynamic and mass transfer properties in detail for the system involving tributyl phosphate (TBP) used in recycle operations of unused uranium and plutonium in PUREX process [6]. The quantitative comparison between the performance of mixer-settler and disc-and-doughnut Bateman Pulsed column was carried out by Movsowitz et al. [7]. They found that both equipments are comparable in terms of yield, simpler operation, lower entrainment of solvent, less mechanical failures, fewer problems with crud and smaller solvent losses. Suresh et al. [8] have used tri-*n*-butyl phosphate (TBP) and tri-sec-butyl phosphate (TsBP) for the separation of U/Th in a counter-current mixer-settler having 16-stages. They used air-pulsed ejector fitted in each cylindrical mixer connected with a short diffuser, fixed at the bottom of the mixer compartment. The mixing device is isolated from the rest of mixer volume except through the diffuser. Laskorin et al. [9] reviewed the extractors for the recovery of uranium and rare metals. It describes the process of extraction, the design and results of tests box-type mixer-settlers with mechanical mixing and air mixing. They concluded that box-type mixer-settler extractors are stable in operation, simple to maintain, reliable in design, and highly efficient. Scale-up studies based on the kinetics of uranium extraction process from chloridric leaches using a box type mixer-settler were carried out by Santana and Dantas [10].

Literature survey reveals that there are many reports on the conventional mixer-settler but little attention has been paid to the inert air/gas agitated liquid–liquid contactors CAL-MSU. In the past decade, considerable efforts have been expended on improving the design of mixer-settlers and increase in throughput per unit volume without introducing interstage pumping. Similarly, many

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Nomenclature

a	specific interfacial area (m^3/m^2)
B	breadth of the mixer of the single stage of the MS unit (m)
$C_{c,in}$	concentration of TBP in continuous phase at the inlet of the CAL-MSU ($mole/m^3$)
$C_{c,in}{}^*$	equilibrium concentration of TBP in continuous phase at the inlet of the CAL-MSU ($mole/m^3$)
$C_{c,N}$	concentration of TBP in continuous phase at the (N) th stage of the CAL-MSU ($mole/m^3$)
$C_{c,N-1}$	concentration of TBP in continuous phase at the ($N-1$)th stage of the CAL-MSU ($mole/m^3$)
$C_{c,N-1}{}^*$	equilibrium concentration of TBP in continuous phase at ($N-1$)th stage of the CAL-MSU ($mole/m^3$)
$C_{c,out}$	concentration of TBP in continuous phase at the outlet of the CAL-MSU ($mole/m^3$)
$C_{c,out}{}^*$	equilibrium concentration of TBP in continuous phase at the outlet of the CAL-MSU ($mole/m^3$)
D	diameter of impeller (m)
E_c	Stage efficiency
H	height of the mixer of the single stage of the MS unit (m)
K_ca	overall volumetric mass transfer coefficient (s^{-1})
M	gas molecular weight (kg/mol)
MTC	mass transfer coefficient
n	agitation speed (s^{-1})
N	stage number
N_p	power number (for Ruston turbine impeller Np = 5)
P_g	power input to the liquid phase in an air sparged system (W)
P_{imp}	power input to the liquid phase in mechanically agitated system similar to CAL-MSU (W)
Q_c	continuous phase flow rate (LPH)
Q_d	dispersed phase flow rate (LPH)
Q_g	gas flow rate (m3/s)
R	gas constant (J/mol K)
R	phase flow ratio (Qc/Qd)
T	absolute temperature (K)
T	width of the mixer of the single stage of the MS unit (m)
v_0	actual superficial gas velocity through nozzle (m/s)
V_M	volume of mixer (L)
V_T	total volume of CAL-MSU and similar pump-mix mixer-settler (m^3)

Greek symbols

ε	fraction jet energy transmitted to bulk (0.06)
ξ	dimensionless concentration (concentration of TBP in continuous phase at the outlet of the CAL-MSU/initial feed concentration)
π	absolute pressure (N/m^2)
π_0	pressure at sparger (N/m^2)
ρ_g	gas density (kg/m^3)
χ	% extraction; $(1-\xi)\times 100$

Subscript

c	aqueous continuous phase
d	organic dispersed phase

new units have been reported in an attempt to overcome above problems in nuclear industry. CAL-MSU device is a stable, reliable, versatile and possesses inherent compactness for efficient operation over a wide range of throughput conditions offering considerable advantage in various applications. In the past very few times it has been used and reported i.e., CAL-MSU used for organic treatment application of uranium–thorium extraction and stripping in 5% TBP-nitric acid system [11].

PUREX process in nuclear fuel reprocessing basically incorporates the liquid–liquid extraction as a central unit operation from front-end to back-end facilities [12] where TBP diluted with range of paraffinic solvents is used as extractant in extraction cycle [13,14]. The organic stream (TBP diluted with paraffinic solvent) has mutual solubility in the aqueous acidic streams and therefore traces of TBP are retained in aqueous stream depending on acid concentration. The traces of TBP in aqueous streams are undesirable and must be removed due to environmental constraints.

We recently carried out detailed mass transfer studies for the removal of TBP from aqueous stream in a geometrically optimized pulsed sieve plate extraction column [15]. Pandey et al. [16] studied the removal of dissolved TBP from aqueous solution by diluent wash method using 6-stage high efficiency ejector mixer-settler. They found that maximum 3 stages of mixer-settler unit were sufficient enough to remove most of the dissolved TBP from the aqueous solution. Manohar et al. [17] have carried out process development studies in CAL-MSU for the removal of dissolved TBP from acidic solutions using dodecane as extractant. These studies have revealed that the concentration of dissolved TBP in 0.3 M HNO_3 can be reduced from ~150 ppm to ~15 ppm using 3.6% TBP in dodecane. However, the systematic approach to evaluate effect of phase flow ratios on the stability and stage requirement study is not considered. Moreover, they did not consider the mass transfer coefficient and power requirement to compare the efficiency at the operating conditions.

Therefore, the present research work involves the systematic experimental study of extraction of TBP from aqueous waste by using NPH as solvent in CAL-MSU. NPH was considered as an extractant as it is cheaper than dodecane. The main objective was to optimize the operating conditions i.e., continuous to dispersed phase flow ratio for the optimum utilization of solvent. As the energy requirement for the system similar to CAL-MSU has not been well reported in literature; the comparison of the power input requirement for CAL-MSU and similar configuration pump-mix mixer-settler is also presented.

2. Material and method

2.1. Materials

TBP with a minimum purity of 99.99 % was purchased from S.D. Fine Chemicals Pvt. Ltd., Mumbai for the preparation of feed solution. NPH and 0.3 M nitric acid solution (industrial grade) were purchased from T.A. Corporation Ltd., Mumbai. NaOH was procured from the Ami Chemicals Pvt. Ltd., Mumbai with 99.98 % purity and was used for the preparation of 0.3 N NaOH solution. Acetonitrile and methanol (HPLC grade) with 99.99% purity were purchased from S.D. Fine Chemicals Pvt. Ltd., Mumbai, India for analysis purpose. Metering pumps of Fluid Metering Inc., USA, were used for precisely pumping the aqueous feed and organic extractant after prior calibration. The system used for study was 0.3 M HNO_3–TBP–NPH and inlet physical properties and feed preparation method for the same is given in Lade et al. [15].

2.2. Analytical method

High performance liquid chromatography (HPLC) and gas chromatography (GC) were used for the analysis of TBP in continuous and dispersed phases, respectively. The detailed