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Nanoemulsion for nanotechnology, size-controlled synthesis of Pd (II) nanoparticles via nano emulsion liquid membrane

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ABSTRACT

Palladium nanoparticles with low polydispersity were fabricated via emulsion globules of various sizes with same sauter mean diameter has been proposed for this purpose. In this paper, the important variables affecting sauter mean diameter of the emulsion drops, including injection method of emulsion, stirring speed, oil phase viscosity, composition of inner water phase and solute permeation rate are also systematically investigated of HCl/Co(III)dicarbolide/xylene/HCl forming $(PdCl_4)^{-2}$ in the presence of Span 80/85 as the surfactants. The particle size, ranging from 3.2 to 4.2 nm, was optimized be controlled by variation of the surfactant, the agitation time and the concentrations. Nano-emulsions were prepared using the spontaneous emulsification mechanism as non-equilibrium systems. XRS,SEM and surface area were used for analysis and the optimized coditions of nanopalladium was 2.5, 1.1 and 0.1 for O/S,glouble diameter and polydispersity respectively. The studies on optimization methods for nano-emulsion gloubles be a required.

KEYWORDS

Emulsion liquid membrane;
Gloublesize;
Nano palladium;
polydispersity.

INTRODUCTION

Palladium is used in jewelry in dentistry[1,2] and production of surgical[3] instruments. Palladium is also used to make professional transverse flutes[4]. The second biggest application of palladium in electronics is making the multilayer ceramic capacity[5]. Palladiums (and palladium-silver alloys) are used as electrodes in multi-layer ceramic capacitors; Palladium (sometimes alloyed with nickel) is used in connector platings in consumer electronics. Hydrogen easily diffuses through heated palladium; thus, it provides a means of purifying the gas[6]. Membrane reactors with Pd membranes are therefore used for the production of high purity hydrogen. A large number of carbon-carbon bond forming reactions in organic chemistry are facilitated by catalysis with palladium compounds. The largest use of palladium today is in catalytic converters[7]. In addition palladium, when dispersed on conductive materials, proves to be excellent electro catalysts for oxidation of primary alcohols in alkaline media[8]. These recent applications have made that studies on optimization methods for nano-emulsion preparation of palladium be required. This work is focused on the most recent developments of nano-emulsions as fi-

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nal application products and on the optimization of their preparation. Nano-emulsions consists of fine oil-in-water dispersions, having droplets covering the size range of 100–600 nm. In the present work, nano-emulsions were prepared using the spontaneous emulsification mechanism which occurs when an organic phase and an aqueous phase are mixed. The organic phase is a homogeneous solution of oil, lipophilic surfactant and water–miscible solvent, the aqueous phase consists on hydrophilic surfactant and water. An experimental study of nano-emulsion process optimization based on the required size distribution was performed in relation with the type of oil, surfactant and the water–miscible solvent. The results showed that the composition of the initial organic phase was of great importance for the spontaneous emulsification process, and so, for the physico-chemical properties of the obtained emulsions. First, oil viscosity and HLB surfactants were changed, the most viscous oil, gave the smallest droplets size (16 ± 2 nm), HLB required for the resulting oil-in-water emulsion was superior to 8. Second, the effect of water–solvent miscibility on the emulsification process was studied by decreasing xylene proportion in the organic phase. The solvent–xylene proportion leading to a fine nano-emulsion was fixed at 10% of membrane. This phase of emulsion optimization represents an important step in the process of nano size droplet by spontaneous emulsification. In the separation process using emulsion liquid membranes, the polydispersity affects mass transport of metal ions from the external phase to the internal phase because under steady operating conditions, drop size and size distribution are proportional to the interfacial area. The present study aims to assess the optimized conditions nano size of emulsion globules. An advancing reaction front model considering. The work divided in two parts, first part the optimized conditions of preparation for palladium, and the second part is the suitable conditions for pertraction of palladium. The modeling of transport of cations was achieved by advancing stripping model[9]. The carrier mediated transport from high salt content using TBP as membrane was done[10,11].

EXPRIMENTAL

Nanoemulsition

The formation properties and applications of nano-emulsions are referred as mini emulsions, ultrafine emulsions, and submicron emulsions)[12-15]. Nano-emulsion droplet sizes fall typically in the range of 20–200 nm and show narrow size distributions. The most publications on either oil-in-water (O/W) or water-in-oil (W/O) nano-emulsions report their formation by dispersion or high-energy emulsification methods.

Nano particles and experimental design

These materials are prepared for permeation metal ions followed by HCl to yield $(PdCl_4)^{-2}$ in stripping phase to yield palladium metal nanoparticle at the end of the process. The size of such particles depends on the number of metal ions initially loaded into the globules r[16]. An orthogonal 24 factorial central composite experimental design with 6 star points (I= 1.68) and 6 replicates at the center point, all in duplicates, resulting in a total of 20 experiments were used to optimize the chosen key variables for the extraction of palladium. The experiments with different agitation speeds are 13000-17000 rpm and M/E ratio 0.1-0.5 M and different carrier concentration 0.01-0.2 M of Co(III)dicarbolide of employed simultaneously covering the spectrum of variables for the percentage extraction of palladium in the Central Composite Design. In order to describe the effects of agitation speed (X_1), M/E ratio (X_2) and carrier concentration (X_3) on percentage of palladium extraction, batch experiments were conducted.

Variables emulsion properties measured. For production of Pd nanoparticle by ELM. The first step is the use of emulsion liquid membrane cell. The second step is using the (F+M). The third step is separation of Feed from membrane. The forth step is de-emulsioncation of membrane (M) by electric charge using electric charge pistole. The fifth step is separation of strip from organic. The sixth step is heating and drying the stripping phase using a heater till 300^0C to obtain Palladium nanoparticles and investigated by X-ray and SEM instruments. Figures (3-5). The treatment combinations and responses of

TABLE 1 : Full factorial design matrix of screening experiments and mean droplet diameter measured

Run	%Span80/85	O/S	Addition time(min)	Agitation rate(rpm)	Droplet diameter(nm)
1	0.09 0.1	1.0	1	14000	15.085
2	0.1	1.0	1	14400	16.05
3	0.2	2.0	1	15000	20.05
4	0.3	2.0	2	16000	23.45
5	0.4	2.0	2	16500	18.1
6	0.8	2.0	2	17000	25.45
7	1.5	2.5	2	16000	24.65
8	2	2.5	3	14000	26.55
9	2.5	3.0	3	14000	28.3
10	2.8	3.0	4	16000	42.05
11	3	3.5	5	16000	48.15
12	3.2	3.5	5	16000	60.655
13	4	2.5	5	16000	29.38
14	4.5	2.5	6	15000	35.48
15	5	3.5	6	14000	42.618
16	5.5	3.5	6	14000	45.65

TABLE 2 : Experimental field for a design matrix

Run	%Span80/85	O/S	Droplet diameter	polydispersity
1	4.51	2	12.16	1.5312
2	4.51	3	17.45	2.6576
3	5.12	2	9.7	1.0296
4	5.12	3	16.06	1.0296
5	4.38	2.5	14.8	1.98
6	5.25	2.5	14.16	1.1792
7	4.82	1.79	7.6	0.8096
8	4.82	3.21	14.82	1.2584
9	4.82	2.5	11.1	1.1528
10	4.82	2.50	11.1	0.100
13	4	2.5	16	29.38
14	4.5	2.5	14	35.48
15	5	3.5	14	42.618
16	5.5	3.5	14	45.65

two central composite designs that Powder. XRD patterns of samples were recorded with a SHIMADZU XD-D1 Diffractometer using Ni-filtered CuKa radiation (k = 1.5406 A °) with the scan rate of 0.1/s. TEM analysis was carried out using a Philips CM12 TEM working at a 100 kV accelerating voltage. Samples for TEM analysis were prepared by dispersing Pd nanoparticles in ethanol followed by drop-casting on a copper grid (400 meshes) coated with car.9-F+M MMM F+M 13-O,11,12-S, 10-F part A-part-B.

Experimental part for kinetic pertraction

Co(III) dicarbolide/xylene, the surfactants of Liquid Emulsion Membrane SPAN 80 and 85 (sorbitol mono-and trioleate) and/other chemicals were analytical grade. A turbine type impeller was used for preparation of the liquid membrane with organic; water volume ratio (r_1 = 1) and at a mixing rate (4000 – 6000) rpm for (5 – 10) min. Some emulsions re-

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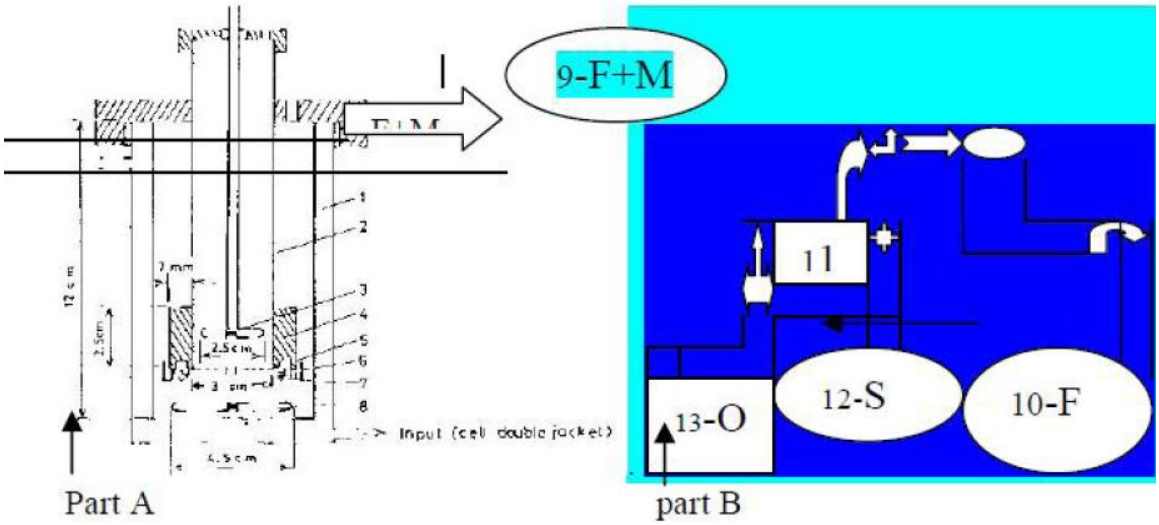

Figure 1 : Scheme of pertraction apparatus for production of Pd nanoparticle by ELM: (1)double shield glass outer vessel, (2) Plexiglas inner tube, (3)Teflon cross stirring blade, (4) Teflon holder, (5) silicon rubber ring, (6) niobium holder, (7) titanium holder, (8) magnet,(9)-F+M(feed, membrane),(11)-electric charge pestol,(12-S),(13-O), (10-F)-solvent

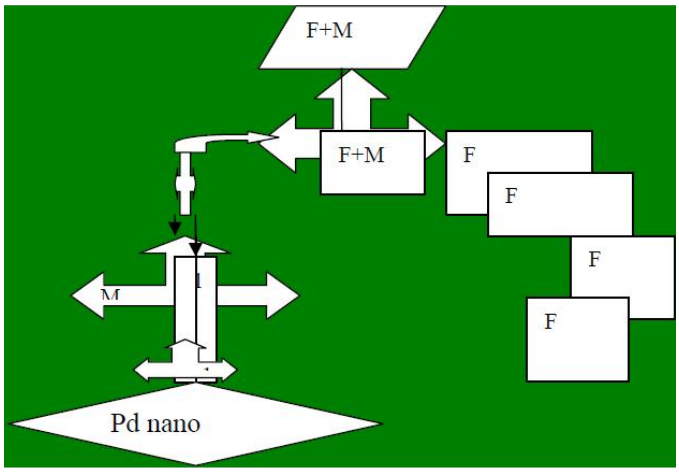

Figure 2 : Flow chart for cell design for production of Pd nanoparticle by ELM

mained stable for months. When breakage of emulsions was desired alcohols were used. The extraction of multiple W/O/W emulsion was performed in a multi stages double-Jackets cell thermo stated temperature 25°C by stirring with magnetic bar (50x10 mm) stirrer at (300-700) rpm usually with 50 ml of outer (feed) solution. The extraction was followed by sample taking (0.5-1.0ml) from solution and measuring by the Atomic absorption spectroscopy type. Atomic absorption/Emission Spectrophotometer/ 210/VGP, Buck Scientific, USA, was used for determination of palladium concentration. The pH values were measured using a pH –meter of the type B-417 HANA. Instrument. Hydrogen ion concentrations in solutions. The deviations in the readings were in the range of ±0.02 at the laboratory temperature 25±2 °C the cell used in pertraction of nano palladium metal using ELM is shown. This design is repre-sented by a second-order polynomial regression model, Eq. (1), to generate contour plots:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_{11}x_{2\,1} + b_{22}x_{2\,2} + b_{12}x_1x_2 + \varepsilon. \qquad (1)$$

RESULTS AND DISCUSSION

Characteristics and properties of nano-emulsions, as non-equilibrium systems depend not only on composition but also on the preparation method. Although interest in nano-emulsions was developed since about 20 years ago, mainly for nanoparticle preparation, it is in the last years that direct appli-

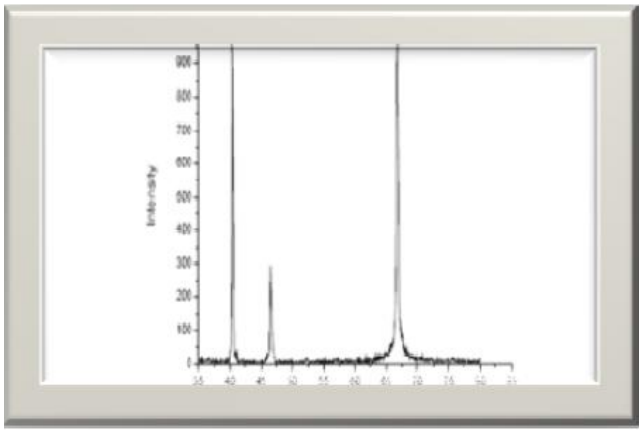

Figure 3 : XRD spectra of palladium before using ELM nano particles

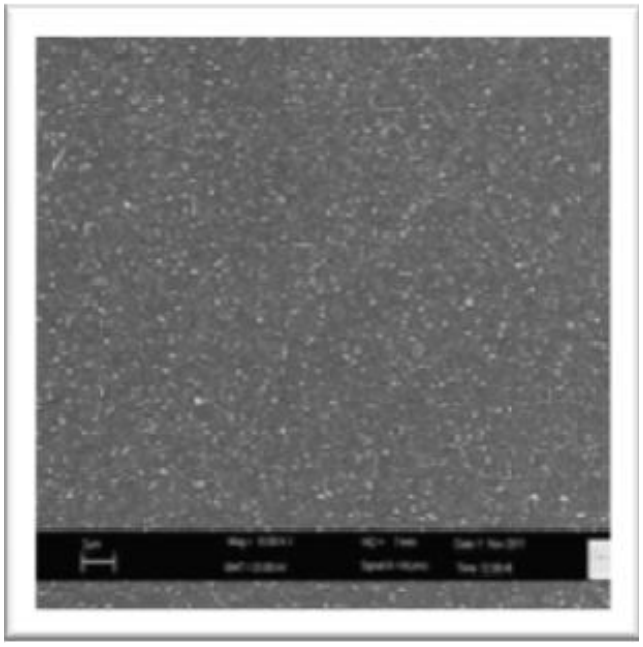

Figure 5 : SEM image of palladium after using ELM

cations of nano-emulsions in consumer products are being developed, mainly in pharmacy. These results were made for studies on optimization methods for nano-emulsion preparation is necessary[12].

Preparation of nano particles from nano emulsion

Palladium chloride ($PdCl_2$) nano-particles with $Pd/PdCl_2$=65:35 % were prepared by an emulsion technique under mechanical agitation without the aid of any surface-active agent. SEM images of black particles are shown in Figures 4 and 5. Aggregates of irregular-shaped particles are observed and the size of Pd particles varies from 4 to 33 nm. A

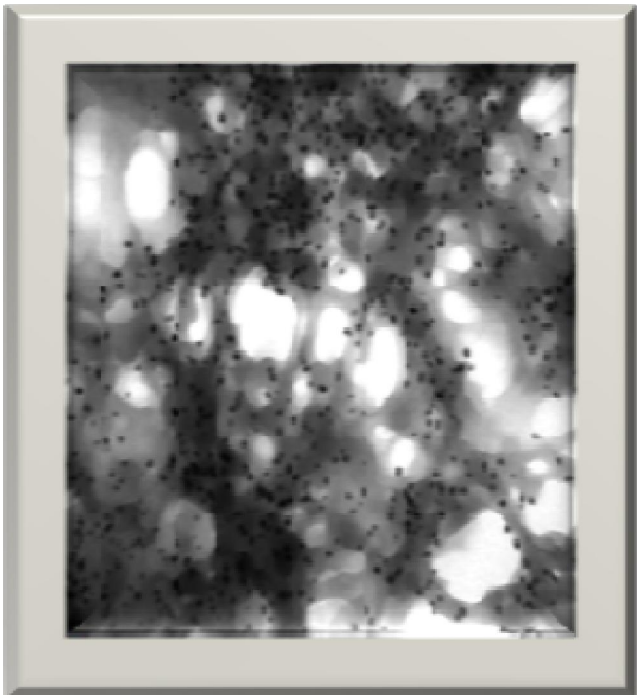

Figure 4 : SEM image of palladium nanopartical 25-120 range particales with a mean size of 60 nm.

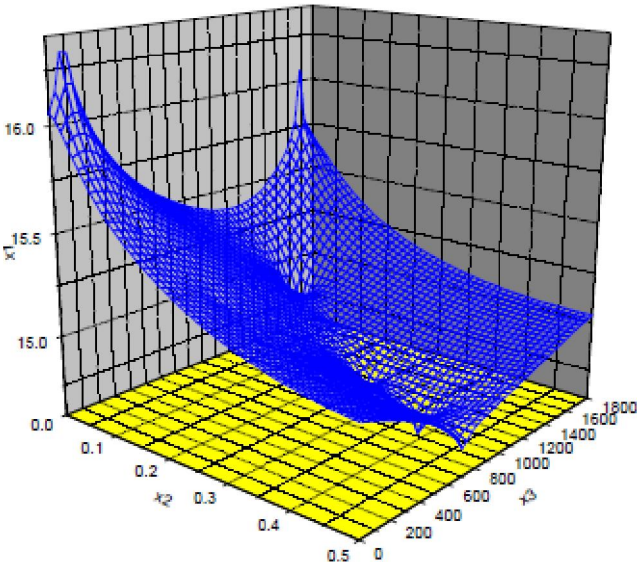

Figure 6 : 3=D optimization plots

nanoparticle also is observed in SEM image as shown in Figures 1 and 5 before and after preparation of nanoparticles of palladium. Hence, it was difficult to calculate the particle size distribution from SEM images. The Figure 3. Is indexed to be corresponding to (112), (2020), (218), (309), (329) and (418). of Pd metal. Powder XRD pattern of Pd nanoparticles is shown in Figure (2). the d-spacing corresponding to XRD lines are 1.986, 1.888, 1.299,

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1.099 and 1.098 A °. These d-spacing values correspond to (111), (200), (220), (311) and (222) planes [13-16]. Particle size analysis showed a narrow distribution of 25–120 nm range particles with a mean size of 60 nm, thus, confirming their nano-structured nature. nano-particles of palladium powders were prepared at a significantly low temperature. From the above optimization process different parameters were studied for preparation of nanoparticles and the different parameters were studied as in Figures 1,2 and 3. Figure 3. XRD spectra of palladium nanoparticles Figures 4, 5. SEM image of palladium before and after using ELM. at 20æ%C and pH=4. The optimization of three parameters as 3-D was shown in Figure 6 (X_1), M/E ratio (X_2) and carrier concentration (X_3) and the plotting of two dimensional contour plots Figure (7).

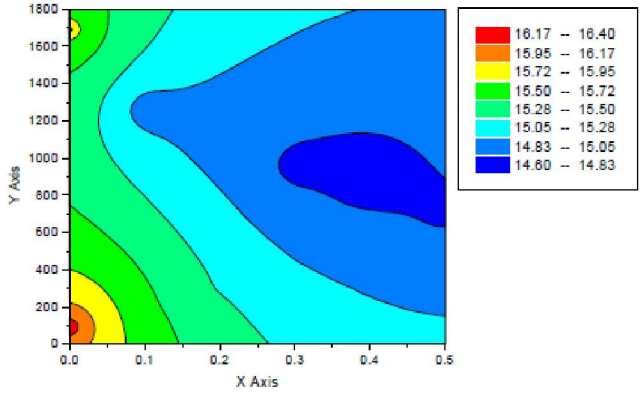

Figure 7 : The contour plot.s of (X_1), M/E ratio (X_2) and carrier concentration (X_3)

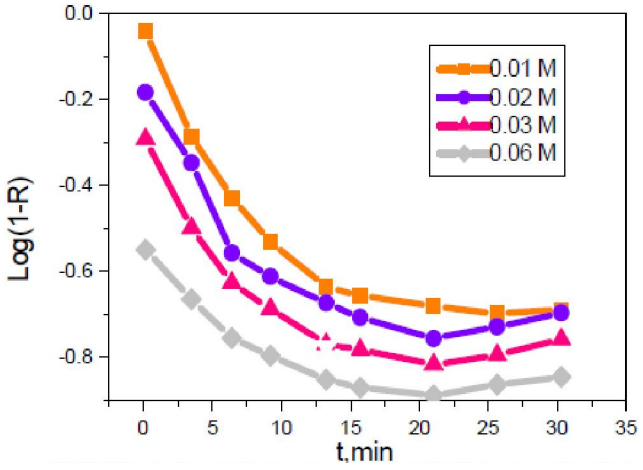

Figure 10 : Effect of stripping phase concentration on pertraction of pd2with emulsions of H+1(B)2in xylene,F=0.01M HCl+0.001M NaCl,0.01M of pd+2,M=0.1M H+1(B)2,3%SPAN,80/85,(3:1), S=xM HCl

Kinetic study

At a constant interface area in double emulsion system and when the concentration of separated element in feed solution is much lower than the concentration of carrier in membrane and their chemical interaction does not change the concentration of carrier at interphase substantially, most of the results on membrane extraction (pertraction) can be approximated by a pseudo-first order kinetic law[11].

$$\log(1-\frac{R}{R_\infty}) = -kt \qquad (1)$$

or

$$R = R_\infty(1-e^{-kt}) \qquad (2)$$

Where R is the fraction yield of pertraction.

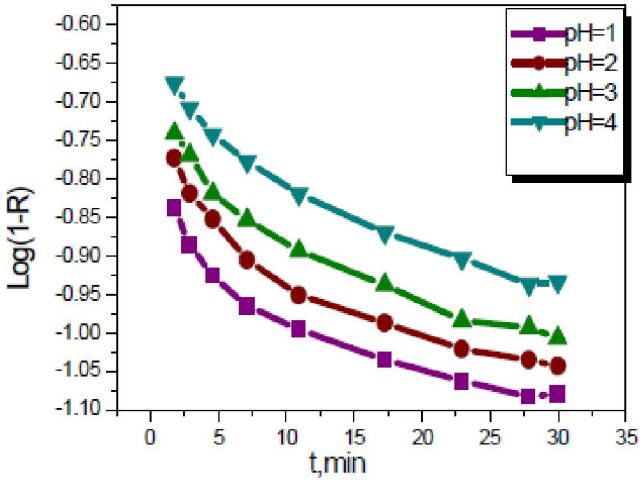

Figure 9 : Effect of membrane phase concentration on pertraction of pd2with emulsions of H+1(B)2 in xylene, F=0.01MHCl+0.01M NaCl, 0.01Mof pd+2, M=x0.1MH+1(B)2, 3%SPAN,80/85(3:1) S=0.03 MHCl

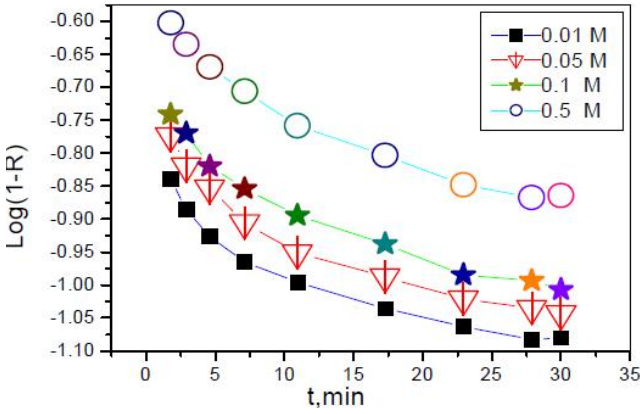

Figure 8 : Effect of pHon pertraction of pd2with emulsions of H+1(B)2in xylene, F=0.001MHCl +0.01NaCl,0.01Mof pd+2,M=0.1MH+1(B)2,3%SPAN, 80/85,(3:1), S=0.03MHCl

K is the rate of pertraction $min^{-1.}$

Influence of aqueous phase acidities

Influence of the feed solution acidity from pH(1 to 4). Figure 8. dipicts the effect pH on the extraction of nano particle of Pd(II),it is found that as the pH increases the pertraction of palladium increases and the maximum yield reached at pH=4.

Effect of membrane phase

Figure (9) Show the influence of membrane concentration from (0.01M - 0.06M HCl) on the pertraction of Pd (II), as the membrane increases, the extraction yield increases. Till 0.95 at 0.01M..

Effect of stripping phase

Figure (10) Shows the influence of strip concentration from (0.01M - 0.5M HCl) on the pertraction of Pd (II). It is interesting to note that the effects of changing strip concentration on the transport of Pd [II] achieve to obtain 99%of pertraction yield were different.

CONCLUSION

The of preparation of palladium by Co(III) dicarbolide from aqueous feeding solution to yield nano particles of palladium in the globule of stripping phase was a chivied and can be studied via optimization at different surfactant concentration, the agitation speed and emulsification time to use nano particles of palladium for pharmaceutical industry. It is found that the emulsion stability was carried out by varying surfactant concentration, agitation speed and emulsification time. The optimum process conditions for the extraction of palladium 1500 rpm, M/E ratio–0.75% (v/v) and carrier concentration 5% (v/v). In nano of ELM, palladium can be optimized through size control of the globule size nano emulsion for nanotechnology. A size-controlled synthesis of Palladium nanoparticles via nano emulsion liquid membrane, ELM, was succeeded. Criterion will depend on particular weight adjudged to either recovery yield, reactants cost and time of performance. There are maxima on neither partial global criterial functions, just local minimum (worst performance) should be avoided to make the process reasonable. A Nano particle size pertraction of palladium was optimized using ELM technique and the effect of different parameters such feeding, membrane and stripping phases were studied. The 3-D optimization and contour plot predict conditiones of preparation of nanoparticles of palladium.

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