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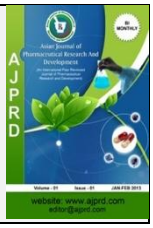

Open Access **Research Article**

Treatment of Waste Whey by Solvent Sublation Method

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A B S T R A C T

Whey liquid is produced in large amounts all over the world every day, this liquid has a high biochemical oxygen demand due to which it creates a serious problem named pollution. But if the liquid is treated beforehand the problem can be overcome. While there are several conventional techniques to treat the liquid before dumping, still they are not as efficient as the solvent sublation method. However, this method is not widely studied yet for large-scale applications. In this study, our objective was to determine the effect of several factors which can alter this method's efficiency e.g. pH, Gas flow rate, volumetric flow rate, the concentration of feed, etc. We discussed in which conditions the solvent sublation process will give its maximum efficiency. This study will not only help in wastewater treatment but also for the separation of molecules of interest from a solution.

Key Words: Solvent sublation, Whey liquid, wastewater treatment, separation of molecules.

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INTRODUCTION

Whey is a byproduct of sweet and cheese industries produced in copious amounts, some amount of the whey waste is utilized in dairy products and as animal fodder but rest are discharged into the streams leads to a high wastewater burden. The whey contains organic matter which increases the biochemical oxygen demand (BOD) in water which makes it a potential pollutant[1]. Since a large amount of whey waste is produced every day worldwide, the risk of water pollution is extremely high. There are various methods like ultra-filtration, gel filtration, ion exchange, coagulation, and precipitation is used for recycling or disposing of whey. However, a cost-effective method for isolation and enrichment of whey proteins is of high economic & ecological interest[2]. There is an alternative but less investigated method called solvent sublation which can remove trace amounts of volatile and non-volatile organic compounds from the wastewater. Although this technique is very efficient; handling is simple and expenses are cheap but the large-scale study in this subject is sparse. Thus, the road toward utilization of this technique in the recovery of usable materials and wastewater treatment is long.

SOLVENT SUBLATION

This technique was first explained by sebba[3] as an option for ion flotation. Solvent sublation is a non-foaming absorptive bubble separation technique where enriched materials absorbed by the bubble are collected in immiscible liquids. There are two phases aqueous & organic where the two phases are placed on top of each other, a surface-active agent is also present at the interphase of the two phases. Gas bubbles are generated in the aqueous media which travels upwards toward the organic phase where the bubbles selectively adsorb the surface-active

materials in water (as in any adsorptive bubble process) and transport the material to the organic phase. These transported materials are either deposited on top of the organic phase after the bubble burst at the liquid-air interphase or gets dissolved while making their way through the immiscible phases. The sublate moves across one direction only, to the organic phase[4]. This happens because of several reasons-(a) rapid flow of bubbles towards the upper organic phase from downwards. (b) also, the bubbles that arrive back at the interface from the organic phase are small and thus have little kinetic energy to overcome the interfacial tension. Since the surface of the bubbles contains a zeta-potential, the volume below the interface, therefore, contains many stationary bubbles. The liquid entrapped in these bubbles is pushed to the organic medium by the larger bubbles moving in the same direction from below. When these bubbles burst into the air, the liquid/water surrounding them form globules which then return to the aqueous phase crossing the interphase. Because of the small size of the droplets; a larger area of the organic-aqueous interface is exposed which is likely to form a liquid-liquid equilibrium. However, as the total amount of water in the organic phase is very small, the amount of sublate returns to the aqueous phase is minimal. stationary bubbles at the liquid-liquid interphase protect the water that tends to move down from the organic to the aqueous phase, rather the water is transported back to the organic phase in the form of layers around the other bubbles. This water carries a small amount of sublate with them[5,6]. Finally, a steady-state is attained where the amount of sublate traveling into the organic layer was equal to that carried back across the interface by the returning droplets[7]. The solvent sublation technique has shown promise for the removal of certain types of organic compounds from aqueous systems on a large scale because of the following reasons-

1) The active material needed to be separated is carried by the gas bubbles into the upper immiscible liquid layer without mixing the phases, thus offering high selectivity greater than other flotation techniques. As the minimum part of the aqueous phase comes in contact with the organic phase, the solvent extraction thermodynamic parameters which control the extent of extraction can be defined from the establishment of an equilibrium state. Insolvent sublation technique this equilibrium state can not be achieved in the bulk of the system but only at the organic-aqueous interphase, which can remain virtually immobile if the gas flow rate is kept sufficiently low[8,9]. As a result, this technique is not limited by the equilibrium constant, so the recovery of trace elements can be as high as 100%.
2) The extent of recovery in other extraction processes depends on the ratio of organic to aqueous liquid volume but the solvent sublation technique is independent of this ratio.
3) This technique can easily handle a large volume of aqueous samples thus make it a potential choice for analysis of natural, residual, and marine water for trace elements.

MATERIALS

Commercial Whey was obtained from local sweet shop, Solvent Sublation glass column with frit attachment was supplied by REMCO Ltd. (Height-100 cm, Internal Diameter-8 cm, External Diameter-8.3 cm), Octanol was supplied by MERCK Ltd., Nitrogen(N_2) cylinder with gas flow controller, No-3 Glass Frit with pore size:16-40 micron, Peristaltic Pump with volumetric flow rate controller was supplied by RIVOTEK, Centrifuge apparatus with speed controller (1000-10000 RPM) was supplied by REMI equipments, Stirrer was supplied by REMI equipments, UV-spectrophotometer (Model- ANALAB UV-180), digital weighing balance made by SARTORIUS, Ultrasonic cleaner manufactured by TAKASHI, Whatman No.4 filter paper.

METHODS

Preparation of Processed Whey Filtrate

Commercial whey obtained from the local sweet shop was filtered using a cheesecloth and then the filtrate was poured into centrifuge tubes. It was centrifuged at 5000G for 30 minutes, the supernatant was collected and passed through Whatman No-4 filter paper. The filtrate is then again centrifuged at the same speed for 15 minutes and this process is repeated until it gave a constant OD value at λmax-280 nm. The filtrate was stored in the refrigerator for further usage.

Preparation of Whey Powder from Whey

The filtrate whey sample (40ml) which we got from the previous process was taken in a Petri dish and the Petri dish with the filtrate was kept in BOD at 50o C overnight. The dried filtrate formed a solid layer on the Petri dish which was scraped off by a spatula. The weight of the scraped powder was taken, from the difference of weight (sample and Petri dish after drying) was calculated. Every 40 ml of whey liquid gives 1.25gm of dried whey powder.

Determination of Critical Micelle Concentration (CMC) of Whey

The required quantity of whey powder is weighed and dissolved in distilled water. Then the solution is suitably diluted to obtain the desired concentration range of 100-800 mcg/ml. The surface tension was also measured by using the drop count method and the concentration vs surface tension graph was plotted.

Table 1: Determination of CMC of whey.

Concentration (Mcg/Ml)	Surface Tension (Dyne/Cm)
100	96
150	94
200	92
250	90
300	88
350	86
400	84
450	82
500	80
550	77
600	76
650	75.2
700	75
750	75
800	75

Determination of Percentage Gas Hold Up

For determination of percentage gas holdup, feed is prepared of different concentrations but maintaining the same protein surfactant ratio. The percent gas holdup was measured in a batch of liquid when gas passed through the column. The gas flow was shut off and then measurement of height of the liquid pool was taken. Again height of the liquid pool was measured after shutting off the gas flow. The percentage of gas bubble entrapped in the liquid column was calculated and tabulated as % gas hold up (Table2). Percent gas hold up was plotted against gas flow rate (GFR) in Fig.3. The operating temperature was maintained at 25°C.

Table 2: Percentage Gas holdup

Time (sec)	GFR (cc/min)	SGV (cm/s)	% H at Ci-500 mcg/ml	%H at Ci-600 mcg/ml	%H at Ci-700 mcg/ml
30	200	0.06	0.2	0.3	0.4
45	250	0.08	0.4	0.6	0.8
60	300	0.1	0.8	1.1	1.4
75	350	0.2	1.3	1.7	2.1
90	400	0.3	1.5	1.9	2.3
105	450	0.4	1.6	2	2.5

SOLVENT SUBLATION (Batch Process)

Partition Coefficient was determined using an octanol/water system and the value was found out to be 2.028. Though no substance was found out in octanol the experiment showed a constant decrease in the concentration of protein in the aqueous phase. The apparatus consists of a long column of 1-meter height, fitted by frit at the bottom and by an enlarged solvent chamber at the top. This chamber is fitted with a reflux condenser. The solvent chamber has an inlet, outlet for feed. The main glass apparatus is assembled with a nitrogen cylinder and gas flow rate controller(rotameter). The feed of desired concentration was prepared and the pH of the feed is also adjusted as per requirement. The glass column was then filled with the feed solution. The aqueous solution is filled until 1 cm mark before the top of the column. Then, the enlarged part of the solvent chamber was covered by a glass cover. The required amount of octanol was added into the chamber and an octanol/feed interface was conspicuous. Bubbles of nitrogen gas are passed through the feed at a desired gas flow rate (GFR)[11]. On top of the solvent chamber, a condenser was connected to prevent evaporation. Residual liquid was collected at a fixed interval and analysed immediately. Steady-state concentration was achieved after some time, the whole experiment was continued for 3hours. In the end, the residual liquid left was collected for analysis. The output, input, loss amount, recovery percentage was calculated and tabulated. The following is a typical diagram of solvent sublation process. (Fig 1)

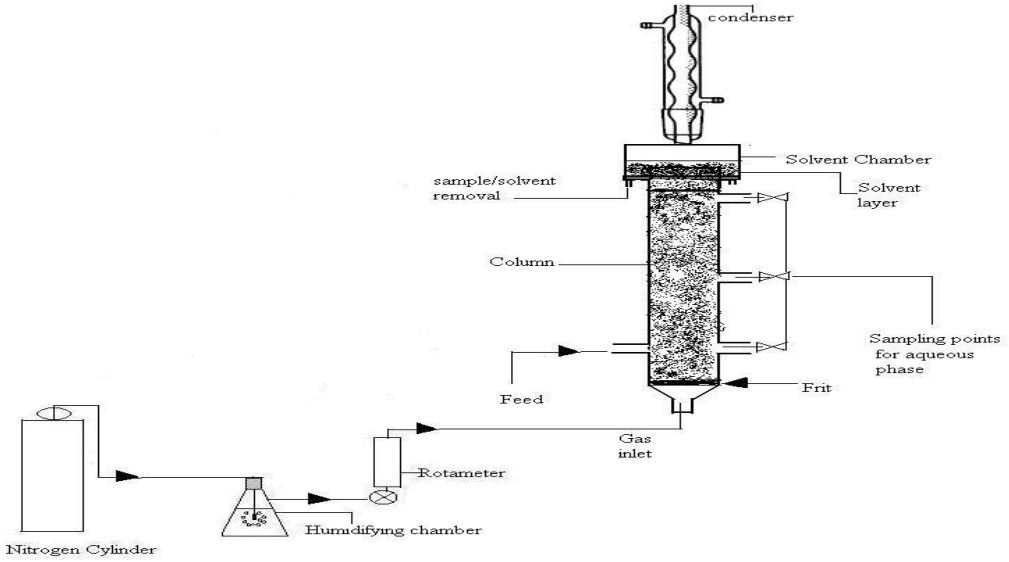

Figure 1: Schematic diagram of solvent sublation apparatus in the batch process

RESULTS

Determination of Critical micelle concentration (CMC)

Here we took different concentrations of the whey liquid (e.g.100, 150,200 etc.) and found the surface tension for individual concentration (table 1). We calculated the CMC from the values as depicted in the fig.2.

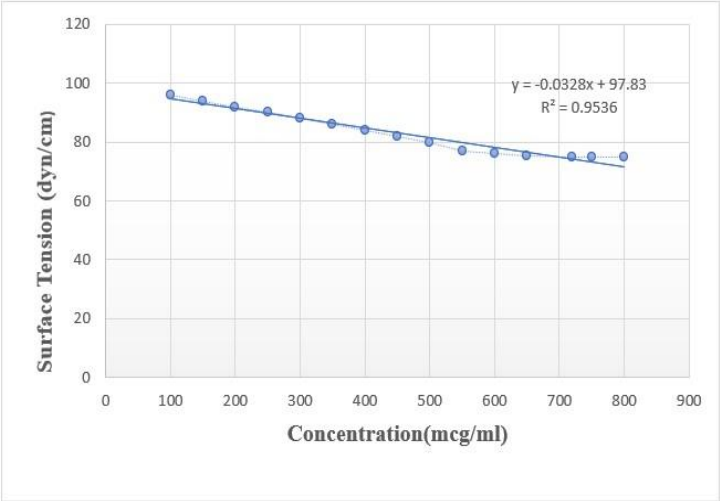

Figure 2: Plot of surface tension vs Concentration of whey

Percentage of Gas holdup

In this portion we saw the gas holdup at different time and when used different gas flow rates (table3) (fig 3).

Table 3: Performance in batch mode at pH=2, Ci=500 mcg/ml, GFR=175 cc/min

Time (min)	Volume of feed sample (ml)	Residual feed volume (ml)	Residual feed concentration (mcg/ml)	Amount in Residual feed (mg)	Amount separated (mg)	% RP	$t_{1/2}$ (min)
30	5	3895	449.5	1750.80	199.20	10.21	146
60	5	3890	394.5	1534.60	415.40	21.30	
90	5	3885	342	1328.6	621.33	31.86	
120	5	3880	287	1113.56	836.44	42.89	
150	5	3875	232	899	1.51	53.89	
180	5	3870	177	684.99	1265.01	64.87	
210	5	3865	174.5	674.44	1275.56	65.41	

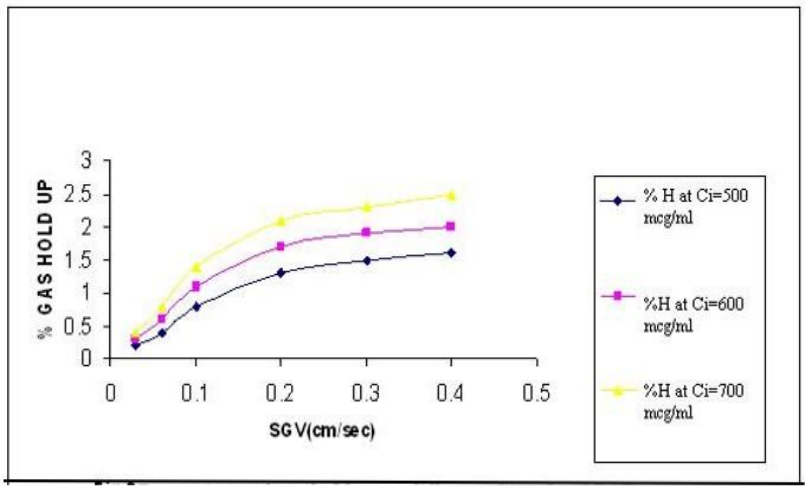

Figure 3: Percentage gas holdup at different Ci at fixed PSR

Performance in batch mode under different pH

- The Ci is kept at 500 mcg/ml, where the pH was 2 and the gas flow rate at 175 cc/min. (Table & fig. 4)
- In the following table (table& fig. 5) the pH is changed to 5 whereas the Ci and GFR values are same as before.
- Again, another criteria was set, the pH is changed to 8 and the other criteria are same. (table & fig. 6)

Table 4: Performance in batch mode at pH=5, Ci=500 mcg/ml, GFR=175 cc/min

Time (min)	Volume of feed sample (ml)	Residual feed volume (ml)	Residual feed concentration (mcg/ml)	Amount in Residual feed (mg)	Amount separated (mg)	% RP	$t_{1/2}$ (min)
30	5	3895	447	1741.06	208.94	10.71	137
60	5	3890	392	1524.88	425.12	21.80	
90	5	3885	332	1289.82	660.18	33.85	
120	5	3880	272	1055.36	894.64	45.87	
150	5	3875	214.5	831.19	1118.81	57.37	
180	5	3870	157	607.59	1342.41	68.84	
210	5	3865	154.5	597.14	1352.86	69.37	

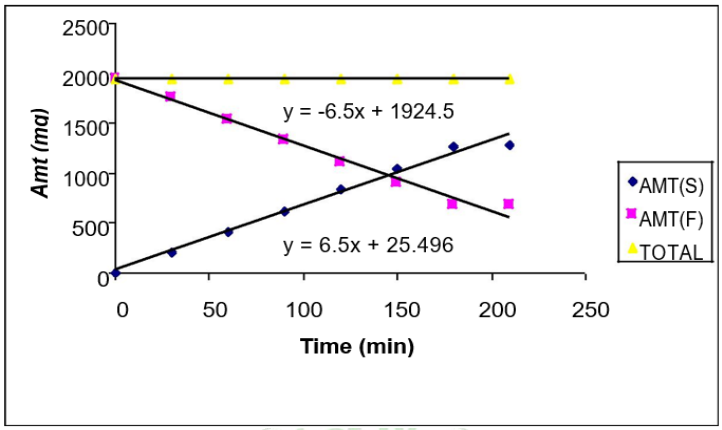

Figure 4: Mass Balance (Ci=500 mcg/ml, GFR=175 cc/min, pH=2)

Table 5: Performance in batch mode at pH=8, Ci=500 mcg/ml, GFR=175 cc/min

Time (min)	Volume of feed sample (ml)	Residual feed volume (ml)	Residual feed concentration (mcg/ml)	Amount in Residual feed (mg)	Amount separated (mg)	% RP	$t_{1/2}$ (min)
30	5	3895	449.5	1750.80	199.20	10.21	157.7
60	5	3890	402	1563.78	386.22	19.80	
90	5	3885	352	1367.52	582.48	29.87	
120	5	3880	299.5	1162.06	787.94	40.40	
150	5	3875	252	976.5	973.5	49.92	
180	5	3870	202	781.74	1168.26	59.91	
210	5	3865	199.5	771.07	1178.93	60.45	

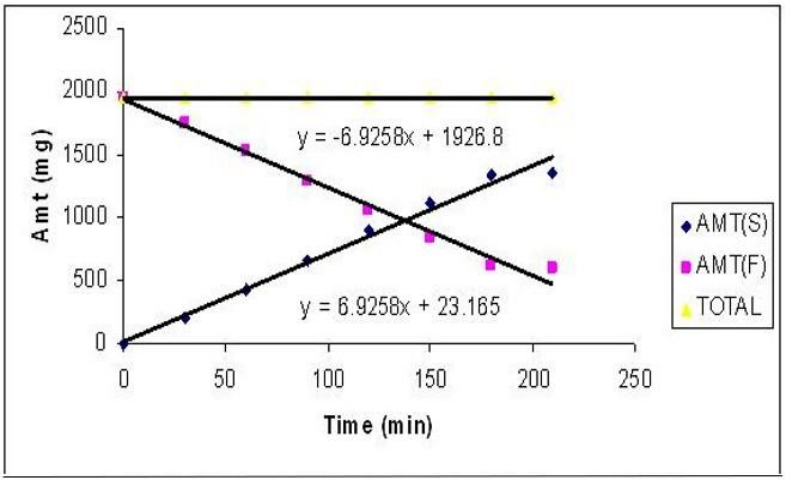

Figure 5: Mass Balance (Ci=500 mcg/ml, GFR=175 cc/min, pH=5)

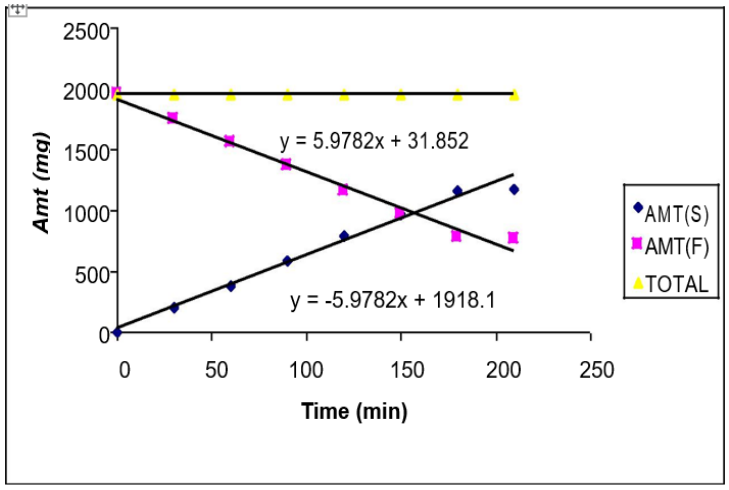

Figure 6: Mass Balance (Ci=500 mcg/ml, GFR=175 cc/min, pH=8)

DISCUSSIONS

This work deals with the separation and removal of whey proteins from commercial whey waste by solvent sublation technique. Several factors such as protein surfactant ratio, pH of the feed, Gas flow rate (GFR), the volumetric flow rate of feed (VFR), Initial concentration of feed (Ci) were studied thoroughly in this work. An effort was made to optimize those various operating conditions so that a maximum separation efficiency can be achieved. The following sections discuss the parameters which altered the results.

Effect of pH of feed on the recovery of whey proteins

From the values, it was found that the recovery process was optimum at pH-5. pH-2 gave less efficient results than pH-5 and pH-8 gave the least value than that of the optimum. The enrichment ratio (Er) (maximum at pH5) increased with the increase in pH and then decreased above pH-5. This happens because of the isoelectric pH of the whey proteins which is around 5, below that it becomes positively charged and at the higher value it becomes negatively charged. Since it is no more ionic (net charge is zero) so it favors interface than the bulk liquid (aqueous). It seems that whey proteins may be separated from bulk due to adsorption of protein in the interface; adsorption of the protein-surfactant complex at pH2 and transportation of some amount of proteins along with the entrained liquid in the foam. This entrained liquid enters foam due to gas flow in the upward direction[10]. The latter causes low enrichment of whey protein.

Effect of gas flow rate (GFR) on recovery of whey proteins

The number of bubbles increases with the increase of gas flow rate (GFR). At a high flow rate residence, the time of bubble within the liquid may not be adequate[12]. The interfacial area also decreases because bubbles coalescence while ascending through the liquid column. At a low flow rate, an insufficient number of bubbles is formed that may not be adequate for sufficient adsorption of protein. In the batch mode of solvent sublation, it was found that enrichment ratio (Er) decreased with increasing GFR (up to 290 ccs/min) at each pH and there is an insignificant change in Er beyond GFR 290 cc/min. An increase of %Rp was observed at pH 2, 5 with the increase of GFR up to 330 cc/min. %Rp did not increase appreciably at GFR above 290 ccs/min when feed pH was 8. In a continuous mode of solvent sublation, range of GFR was 150- 200 cc/min.% Rp increased with the increase of GFR up to 175 cc/min and then it decreased at 200 cc/min. At high GFR bubbles, coalescence and decrease in the interfacial area caused low %Rp. Therefore, GFR at 175 cc/min was found suitable. From the results, we saw that the performance criteria were highest at a GFR of 175 cc/min in the solvent sublation process.

Effect of concentration of feed on the recovery process of whey

From the results, we interpreted that maximum recovery was obtained at the initial feed concentration of 500 mcg/ml. At PSR 1.5 both % RP and Er increased with the increase of Ci up to 500 mcg/ml. When Ci was greater than 500 mcg/ml, low %RP and Er were observed. We saw that the adsorption becomes stagnant at high Ci, therefore it is obvious that %RP will be lesser at Ci-600 mcg/ml because sodium lauryl sulphate (SLS) molecules cannot move adequately to the interface due to excess amount of surrounding molecules of protein.

CONCLUSION

The solvent sublation process is very promising and viable for separation of molecules. In this study we found that if the process is carried out when the pH of the medium is kept no less or more than 5, the gas flow rate at 175 cc/min and the concentration of the feed (ci) at 500 mcg/ml; the solvent sublation technique gives its optimum efficiency. Therefore, we recommend from the results of this study that abiding these values for carrying out this process for laboratory or in large scale would be adventitious.

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