Recovery of Priority Pollutants from Aqueous Solutions through Liquid-liquid Extraction with Simultaneous Treatment of Acid Gases

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In the present work it is studied the recovery of phenol diluted in aqueous solutions (1wt.-%). The process consists of 3 stages: (A) removal of phenol from the aqueous solution through liquid-liquid extraction with butyl acetate (*BA*); (B) removal of phenol of the extract generated in stage (A) through liquid-liquid extraction with chemical reaction with an aqueous solution of *NaOH* (5wt.-%), and (C) recovery of phenol from the aqueous phenolate solution generated in stage (B) through the reaction with CO_2. The stages (A) and (B) are conducted in batch and (C) in semi batch mode of operation. In stage (A) it is studied the removal of phenol from aqueous solutions in an agitated vessel of 5 liters. It is studied the influence of the variables temperature, phase ratio, speed and time of agitation on the global coefficient of mass transfer and efficiency of phenol removal. The values of K_O varied of 3.71E-6 to 8.16E-5 m/s and the efficiencies of phenol removal varied from 45 to 60%. In stage (B) it is studied the removal of phenol from butyl acetate and methyl isobutyl ketone (*MIBK*) in an agitated vessel of 1 liter. It is studied the influence of the variables temperature, *NaOH* concentration, speed and time of agitation on the efficiency of phenol removal. The removal efficiencies varied from 70 to 90%. In stage (C) it is studied the reaction of the CO_2 with aqueous sodium phenolate in an agitated vessel of 1 liter. It is studied the influence of the variables temperature, agitation speed, gas flow rate and composition on the absorption rate of CO_2. The absorption rates varied from 0.4 to 2.5 LCO_2/h.

1. Introduction

The phenol, or hydroxybenzene, and several phenolic compounds are highly toxic and are present in the list of priority chemicals of the Environmental Protection Agency-EPA (Theodore et al., 1997), coming down to 11 phenolic compounds of the 129 substances present in that list. A significant number of organic pollutants found in the environment are phenols (Rosatto et al., 2001) that are products commonly used in industrial processes and, for this reason; they are also frequently found in industrial effluents (Lin et al., 1999). Phenolic compounds are found in the effluents of industries that produce and use phenols, besides cokeries and petroleum refineries. If one considers only the phenolic effluents, the several possible treatment techniques can be divided in two generic groups: destruction and of recovery methods (Saxena and Jotshi, 1996). The liquid-liquid extraction is economically viable for high solute concentrations, above 1000 ppm, and high throughputs (Kentish and Steven, 2001). Due to the rather high phenolic compound concentrations, usually found in industrial effluents, new extraction processes are being tested elsewhere (Juang et al., 2009). The process of recovery of phenols from effluents through liquid-liquid extraction usually

consists of 3 basic operations: phenol extraction, phenol separation from the solvent and solvent separation from the treated effluent (Jiang et al., 2003). The phenol separation from the solvent can be accomplished economically with a second extraction with an aqueous solution of *NaOH*, forming aqueous sodium phenolate. This extraction was not much studied (Binns et al., 1960; Bizek et al., 1992). The liberation of the phenol from the phenolate can be accomplished through the absorption, with chemical reaction, of acid gases (CO_2, SO_2 or H_2S) or any stronger acid than the phenol. The project proposed will allow abating the emission of CO_2 of combustion gases and to avoid the generation of CO_2 when phenolic compounds are incinerated a usual means of treatment of this kind of toxic effluents. The abatement of CO_2 emissions is a very important issue in order to minimize the Greenhouse Effect (Diaz and Navaza, 2009).

2. Experimental Part

A scheme of the experimental equipment is showed in Figure 1. It was constructed according to information contained in the literature (Sada et al., 1977; Quadros and Baptista, 2003; Palma et al., 2007). The agitated tank, A, is made of glass and has a volume of 5L, and a jacket for heating and cooling with water. This tank has an agitator, B, temperature indicator, C, and sampler, D. In the bottom of the vessel there is a valve, E, to collect samples of the aqueous phase. The temperature is controlled by thermostatic baths, F, that allows the temperature control in the range of 10 to 60 C with a precision of 1 C. The agitators, B, J and E, have displays that show the agitation speed in the range of 100 to 1500 rpm. The pH meter, G, and the condutivimeter, H, are used in the aqueous phase. The agitated vessel, and reactor, I, is made of glass and has a volume of 1L, jacket for heating and cooling with water. This reactor has an agitator, J, temperature indicator, K, and sampler, L. In the bottom there is a valve, M, for sampling and withdrawn of the phases. The agitated vessel, N, is made of glass and has a volume of 1L, jacket for heating or cooling. This reactor has an agitator, O, temperature indicator, P, and a submerged pipe to disperse the gas, Q. In the bottom there is a valve, R, for sampling and withdrawn of the aqueous phase and of phenol. The gas is stored in the cylinder, S, and its volumetric flow rate is regulated through the needle valve, T, its temperature is controlled by the thermostatic bath, F, saturated with water in the glass tube, U, and volumetric flow rate indicated by the rotameter, V. The volumetric flow rate of the exit gas is indicated by the rotameter, W. After the rotameter, W, a bubbler, Z, contains aqueous NaOH to retain the remaining acid gases. It can be made samplings of the exit gas through the valve, X, and syringe with needle, Y. The used chemical products are methyl isobutyl ketone and butyl acetate commercial grade furnished from RHODIA S.A.; phenol and NaOH are from MERCK; carbon dioxide, CO2, with purity 99.9% is furnished by WHITE-MARTINS S.A. In all the experiments distilled water was used. All the samples collected in the stages (A) and (B) were analyzed to obtain the phenol concentration in a gas chromatographer VARIAN model CG 3400 CX with capillary silica column CP-Sil 8 CB Low Bleed/MS (CP5862).

3. Results and Discussion

The results of phenol concentration in the organic phase, C_{Phenol}, under unsteady state operation, global coefficient of mass transfer, K_0, and phenol removal efficiency from the aqueous phase, η^A, are shown in Tables 1 and 2 and also in Figure 2, for phase relation (*PR*) 1/5 and 1/10 and temperatures of 35 and 20°C. The phenol concentration

in the aqueous phase and rotational speed were kept constant and equal to 1wt.-% and 200 rpm, respectively.
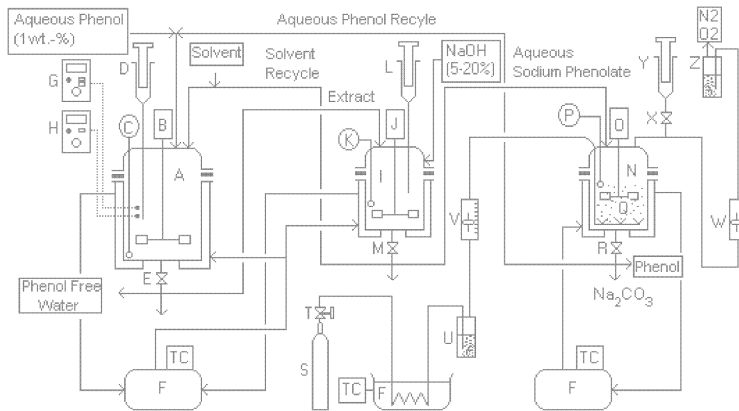

Figure 1 – Experimental Equipment.

The analysis of the results in Tables 1 and 2 shows that the phenol concentration in the organic phase grows with the time of agitation. For run times of about 5 to 10 min. the variation of the concentration is not more significant for the temperatures and phase relations studied. The removal efficiency exhibited a maximum value of 75% for $T = 35°C$ and $PR = 1/5$. This can be explained if one considers that greater values of PR corresponds to a larger relative amount of solvent and the increase of the temperature decreases the viscosities of the fluids, promoting larger turbulence for the same rotational speed. The results for the determination of the dynamic behavior of the extraction with chemical reaction of phenol from butyl acetate and $MIBK$ (initial concentration of phenol 13.2wt.-%) with an aqueous solution of $NaOH$ (5wt.-%) in batch process for two temperatures (20 and 40°C) and fixed rotational speed of 300 rpm are shown in the Table 3 and Figure 3. Through the analysis of the data shown in the Table 3, it is verified that the phenol concentration in the organic phase decreases with the time of agitation and that for run times between 5 and 10 min. the concentration variation is not more significant for the studied conditions. The final removal efficiencies are high and range from 70 to 90%. The influence of the nature of the solvent can be verified through the data shown in Figure 3, for $T = 20$ and 40°C. The results for $T = 20°C$ show that the extraction with $MIBK$ is significantly superior to the extraction with butyl acetate: the final removal is of 72% for the acetate and of 90% for $MIBK$. For $T = 40°C$, the difference between the two solvents decreases, even so, $MIBK$ continues being better than the acetate: the final removal is of 85% for the acetate and of 88% for $MIBK$. This ketone is a better solvent for the phenol extraction because it has $K_D = 110$, while for the acetate, $K_D = 65$, both at infinite dilution. The increase of the temperature provokes the increase of the removal for both solvents and it decreases the difference among them due to the increase of the convective mass transport due to the decrease of the viscosity of the fluids.

Table 1 - Results of phenol concentration in the organic phase (*BA*), global coefficient of mass transfer and phenol removal efficiency from the aqueous phase (*T* = 35°C, *N* = 200 rpm).

	PR = 1/5, K_O=3.7E-6 m/s			*PR* = 1/10, K_O =8.3E-6 m/s		
Run	*t* (min)	C_{Phenol} (%)	η^A (%)	*Run*	C_{Phenol} (%)	η^A (%)
A01	1	1,16	23,1	B01	1,14	11,4
A02	5	3,58	71,6	B02	1,39	13,9
A03	10	2,89	57,8	B03	3,39	33,9
A04	15	3,67	73,5	B04	3,04	30,4
A05	20	3,09	61,9	B05	5,30	53,0
A06	25	3,44	68,9	B06	4,37	43,7
A07	30	3,74	74,8	B07	4,37	43,7

Table 2 - Results of phenol concentration in the organic phase (*BA*), global coefficient of mass transfer and phenol removal efficiency from the aqueous phase (*T* = 20°C, *N* = 200 rpm).

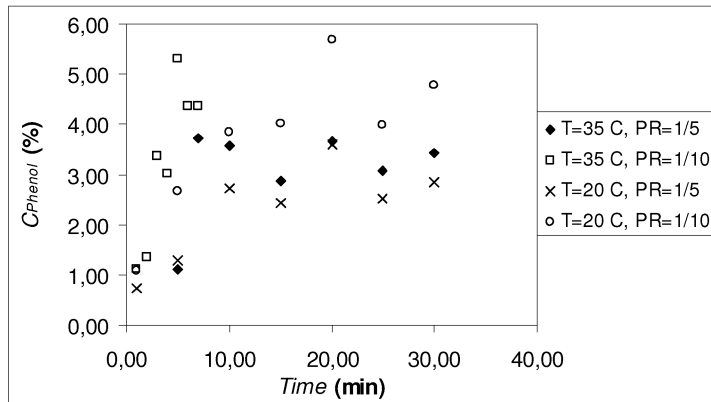|	*PR* = 1/5, K_O=8.2E-5 m/s			*PR* = 1/10, K_O=3.9E-5 m/s		
Run	*t* (min)	C_{Phenol} (%)	η^A (%)	*Run*	C_{Phenol} (%)	η^A (%)
C01	1	0,76	15,1	D01	1,13	11,3
C02	5	1,33	26,5	D02	2,69	26,9
C03	10	2,75	54,9	D03	3,84	38,4
C04	15	2,45	49,0	D04	4,03	40,3
C05	20	3,63	72,6	D05	5,67	56,7
C06	25	2,55	51,0	D06	3,98	39,8
C07	30	2,85	57,1	D07	4,77	47,7

Figure 2 - Dynamic behavior of the process – Stage (A).

The results for the determination of the dynamic behavior of the CO_2 absorption in the agitated vessel operated in semi batch mode, for two temperatures (20 and 40°C) and 3 rotational speeds (100, 300 and 600 rpm) are shown in Figure 4. The volumetric flow rates of the gases were measured at 20°C and P_{atm} = 700 mmHg. The concentration of the phenolate aqueous solution was kept constant and equal to 23,2wt.-%. The volumetric flow rate of the gaseous mixture of CO_2 (75%v/v in N_2) was fixed in 7,0 L/h.

Table 3 - Concentration results, C_{Phenol}, and phenol removal efficiency, η^B, under unsteady state regime.

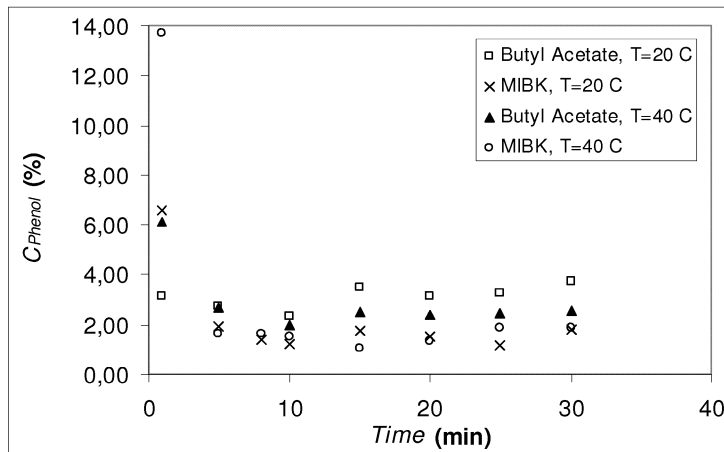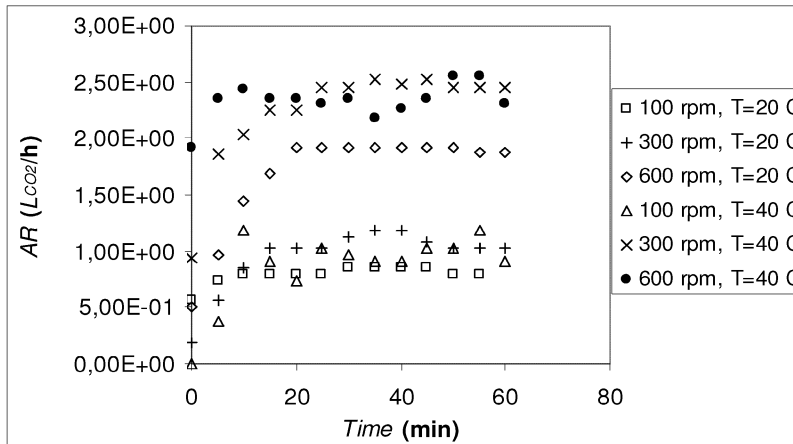| | BA | | | | MIBK | | | |
| | $T = 20°C$ | | $T = 40°C$ | | $T = 20°C$ | | $T = 40°C$ | |
t (min)	C_{Phenol} (%)	η^B (%)	C_{Phenol} (%)	η^B (%)	C_{Phenol} (%)	η^B (%)	C_{Phenol} (%)	η^B (%)
1	3,17	76,0	4,29	67,5	1,94	85,3	1,65	87,5
5	2,73	79,3	3,11	76,5	1,25	90,6	1,52	88,5
10	2,32	82,4	2,92	77,9	1,72	86,9	1,08	91,8
15	3,50	73,5	2,81	78,7	1,50	88,6	1,35	89,8
20	3,15	76,1	4,45	66,3	1,19	91,0	1,89	85,7
25	3,28	75,1	1,61	87,8	1,84	86,1	1,86	85,9
30	3,73	71,7	1,97	85,1	1,38	89,6	1,65	87,5

Figure 3 - Influence of the solvent nature.

Figure 4 - Rate of CO_2 absorption (AR). ($Q_E = 7,0$ L/h)

Through the analysis of the data shown in Figure 4 is verified that the rotational speed exhibits a minor influence for $T = 20°C$ and that it influences the process significantly for $T = 40°C$. We verified that the agitation doesn't influence the process significantly

for 20°C and, in the same way; it doesn't also influence the process for rotational speed of 100 rpm. For the higher temperature the system is sensitive to the increase of the rotational speed, which seems to influence equally for 300 and 600 rpm. With the increase of the temperature from 20 to 40°C the process of mass transfer becomes controlled by the agitation and mixing process in the vessel.

4. Conclusions

The results were, in its majority, very promising for the pursuit of the work, because, for run times relatively short, were obtained high phenol removal efficiencies. The used equipment and the methodology initially developed were satisfactory, what was checked with the analysis of the results, quantitatively coherent.

4. References

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