

THE REMOVAL OF DINITROCHLOROBENZENE FROM INDUSTRIAL RESIDUALS BY LIQUID-LIQUID EXTRACTION WITH CHEMICAL REACTION

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Abstract - Nitrochlorobenzenes (NCBs) are very important in the chemical industry since they have been used as raw material for the manufacture of crop protection products, as active ingredients in the pharmaceutical industry, as pigments and as antioxidants as well as for other uses. In industrial processes, NCBs are produced by monochlorobenzene (MCB) nitration reactions and one of the main residuals formed is dinitrochlorobenzene (DNCB), which is mainly composed of the isomer 2,4DNCB. This subproduct, although of commercial interest when in its pure state, is generally incinerated due to the high costs of recovery treatment and purification. The objective of this study is to present an alternative to the treatment of industrial residuals containing DNCB. The technique consists of converting DNCB into sodium dinitrophenolate, which is very soluble in water and is also easy to reuse. For this purpose, liquid-liquid extraction with chemical reaction (alkaline hydrolysis) with a rotating disc contactor (RDC) is used. Experimental data on MCB nitration reactions as well as alkaline hydrolysis using a rotating disc contactor are presented.

Keywords: Extraction; Reaction; Dinitrochlorobenzene.

INTRODUCTION

In recent years, units that are suitable for chemical reactions and separation operations have attracted the attention of a lot of researchers. Through a combination of separation and chemical reaction processes, notable size reductions have been obtained in the separation units, which has indeed led to a large investment savings. In spite of this, only a few studies on processes of extraction with chemical reaction have been published in the last few years.

For example, DeGarmo et al. (1992) and Doherty and Buzad (1992) considered reactive distillation in the production of methyl acetate and methyl tert-butyl ether and clearly showed the advances and benefits of the combination of separation and chemical reaction processes. Similar advantages were also obtained by Coca et al. (1993) and Tonkovich and Carr (1994) using absorption and chemical reaction simultaneously. Besides these, it is worth mentioning the work of Tsotsis et al. (1993), who used the permeation operation in a membrane reactor, and the work of Sharma (1988), in which

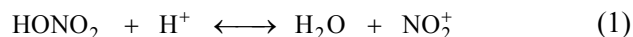
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liquid-liquid extraction in a double-phase reactor was studied.

In extraction with chemical reaction, or reactive extraction, a second liquid phase containing a solvent may be deliberately added to the system. In extraction with no reaction, the solvent extracts a product or an intermediate product; however, when there is chemical reaction, extraction may be considerably quicker, making the process more effective.

Some processes, such as the nitration of aromatics, alkaline hydrolysis and alkylation of organic compounds, are pointed to in the literature as having great importance as processes of extraction with chemical reaction. The process of nitration of aromatics, for example, has been studied for more than three decades (see, e.g. Lo, T.C. et al.), and only during the last decade could the reaction engineering aspects be clearly established. This process involves nitration reactions that are generally conducted in two stages as follows:

1st stage - Formation of the nitronium ion

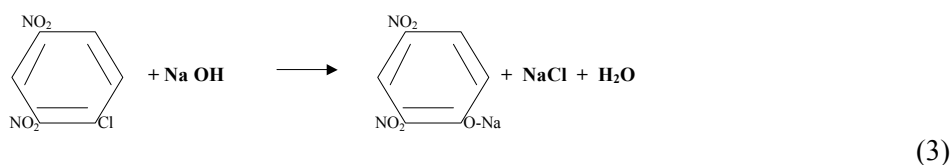


2nd stage – Reaction between the dissolved aromatic compound, ArH, and the nitronium ions



The nitration process is inclusively used in the organochlorinated compound petrochemical industries for the purpose of obtaining ortho and paranitrochlorobenzene, which are used by the pigment industry. In the industrial nitration processes, a residue mainly composed of dinitrochlorobenzene (DNCB), which is difficult to recover and discard in to the environment, is also formed. This residue is generally incinerated, which leads to an increase in the overall process costs.

An alternative to DNCB recovery would be its conversion into sodium dinitrophenolate [$\text{C}_6\text{H}_3(\text{NO}_2)_2\text{ONa}$] through alkaline hydrolysis by the reaction shown below:



Unlike DNBC, sodium dinitrophenolate is sufficiently soluble in water and may also be reused in the processes of pigment manufacture.

At the petrochemical industrial complex in Camaçari, Bahia, the company GRIFFIN Brazil Ltda has been very successful in the development of studies for the purpose of reducing the quantity of DNCB in its residue streams.

The main objective of the present study is the conversion of the DNCB in a mixture of nitrochlorinated compounds into sodium dinitrophenolate using liquid-liquid extraction with chemical reaction (alkaline hydrolysis). The process consists of two steps. Firstly DNCB is obtained through nitration of monochlorobenzene (MCB) in a thermostatic stirred glass reactor. Subsequently, the resulting DCBN is converted into sodium dinitrophenolate through alkaline hydrolysis. In this latter process, a rotating thermostatic disc contactor (RDC) is used along with the aforementioned glass reactor.

EXPERIMENTAL SETUP

The tests conducted in the present study involve MCB nitration reactions and DNCB alkaline hydrolysis. The nitration tests were conducted in a glass reactor, shown in Figure 1, while the hydrolysis tests were conducted both in the reactor and in an RDC, which is sketched in Figure 2. MCB nitration was required in order to obtain the DNCB; this product was then used as the raw material in the alkaline hydrolysis reaction.

Next, details on both pieces of equipment used (the reactor and the contactor) as well as the experimental techniques employed in the tests will be presented.

The Reactor

The glass reactor used in the present work consists of a balloon-shaped glass recipient with four outlets. Figure 1 shows in detail the reactor used in the tests.

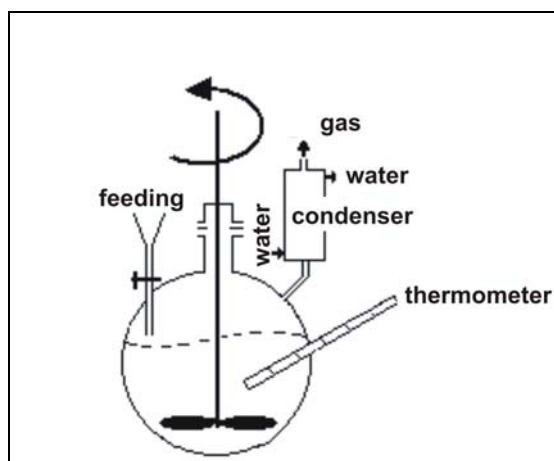


Figure 1: Schematic representation of the reactor (1000 ml) used for nitration and alkaline hydrolysis.

The Rotating Disc Contactor (RDC)

The RDC used in the present work is shown in Figure 2. This equipment consists of a glass column 50 cm in height and 5.0 cm in diameter with temperature control. Inside, a rotating disc and stainless steel rings

stir the liquid mixture. Rotation velocity is controlled with a digital tachymeter adapted to the column shaft, while the outflows of both liquid phases are measured with rotameters. The mixture temperature is kept constant by means of a thermometer and a heating system connected to a thermostatic bath.

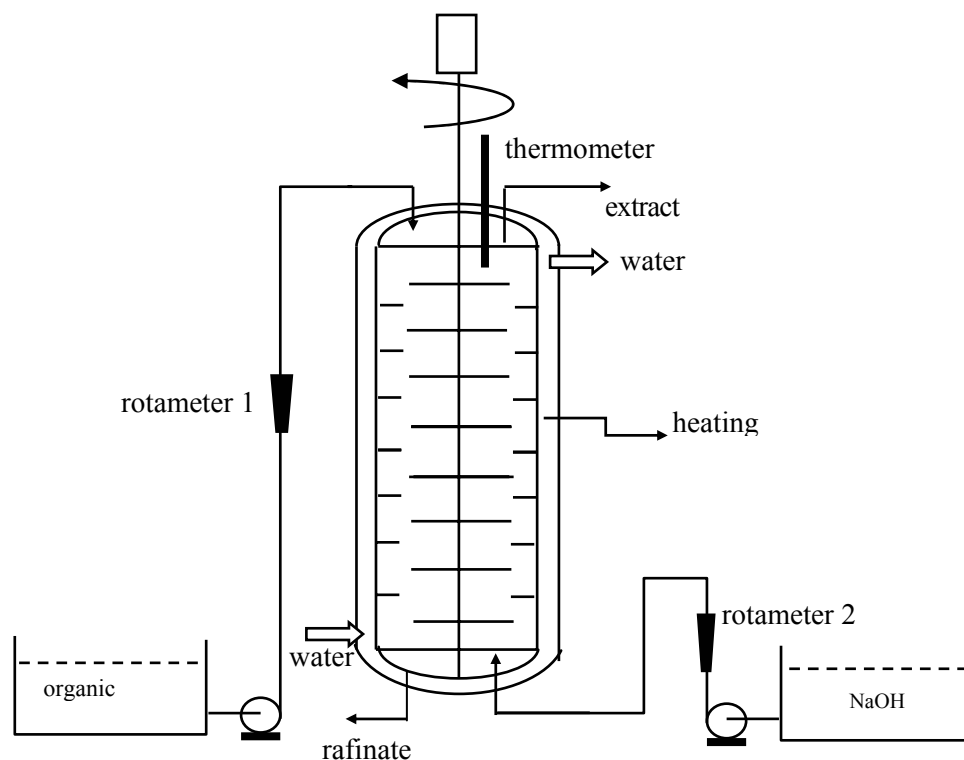


Figure 2: Schematic diagram of the rotating disc contactor (RDC) used in the alkaline hydrolysis.

Chromatographic Analysis

Organic samples were analyzed with a Hewlett-Packard HP5890 gas chromatograph equipped with a flame ionization detector (FID). A 25 m x 0.32 mm x 0.5 μm capillary column of phenyl-methyl-silicone (5.0%) was used and the peak areas were integrated by a Hewlett-Packard 3390A model. Column, injector and detector temperatures were 290°C, 200°C and 300°C respectively. A hydrogen flow of 30 ml/min was used as carrier gas. Synthetic mixtures of known composition had been previously studied for standardization of the analytical method.

Nitration Experiments

In the nitration experiments, reactions of MCB with nitric acid (HNO_3) (equation 3) were conducted with sulfuric acid (H_2SO_4). The purpose of this reaction was to obtain the nitrochlorinated organic mixture containing DNCB that would be used in the alkaline hydrolysis reactions. Thus, a mixed acid ($\text{HNO}_3 + \text{H}_2\text{SO}_4$) was prepared for further reaction with the MCB, thereby conducting the nitration reaction.

In order for the nitration reactions to occur, the reactor shown in Figure 1 was fed with pure MCB and the mixed acid, maintaining the temperature at around 90°C. The reaction was completed within approximately 1.5 hours, with the formation of two different phases inside the reactor. The lower phase contained the organic compounds or the desired organic mixture and the upper phase contained the sulfuric acid, which should be further separated from the mixture. Samples were then taken and analyzed by chromatography.

Alkaline Hydrolysis Experiments

The alkaline hydrolysis experiments consisted of the reaction of the organic mixtures produced in the nitration experiments with sodium hydroxide (NaOH), according to Equation 3, for the purpose of converting the DNCB in the mixture into sodium dinitrophenolate. These experiments were carried out

in both the reactor shown in Figure 1 and in the rotating disc contactor (Figure 2).

a) Alkaline Hydrolysis Using the Reactor

The experimental procedure for alkaline hydrolysis in the reactor was quite simple, since it basically consisted of feeding the organic mixture obtained from the nitration reactions and the NaOH solution into the glass reactor. A mechanical stirrer was used for homogenizing the mixture, while a controlled DC supplier connected to a heating blanket was employed to control the temperature. Samples of the solution formed were collected at one-hour time intervals and analyzed by chromatography.

The experiments were generally finished after 4 or 5 hours, when practically all DNCB had been converted into sodium dinitrophenolate. This occurred when a change in mixture coloration was observed, as confirmed through results obtained from analyses of the samples collected.

b) Alkaline Hydrolysis Using the RDC

Alkaline hydrolysis in the RDC also consisted of organic mixture reactions, namely nitration with NaOH for the purpose of converting DCBN into sodium dinitrophenolate. Unlike the experiment carried out in the glass reactor described in the previous section, all experiments were conducted in a continuous fashion with the temperature kept constant at 90°C. The experimental conditions studied are shown in Table 1.

In these experiments, the contactor was fed at the top with the organic mixture (3.2 g/min) and at the bottom with the NaOH solution (1.0 g/ml). Once the column feeding streams had been adjusted, the temperature (90°C) and the disc rotation velocity (1000 or 2000 rpm) were also adjusted with a thermostatic bath and a tachymeter respectively.

Process stabilization occurred after 5 to 6 hours of operation, when the presence of both phases inside the column was clearly verified. However, samples were collected every 30 seconds for the purpose of progressive visualization of the process of conversion of DNCB into dinitrophenolate.

Table 1: Experimental parameters and ranges of operating conditions.

Parameters	ranges
NaOH outflow (g/min)	1.0
Mixture outflow (g/min)	3.2
NaOH mass fraction (%)	5 to 10
Rotation velocity (rpm)	1000 to 2000
Temperature (°C)	90

RESULTS

The results obtained in the present work consist firstly of data on the synthesis of the nitrochlorinated mixture containing DNCB (nitration reaction). Then, data on the reaction conversion of DNCB into sodium dinitrophenolate, using the glass reactor and the RDC, are presented. The results of the monochlorobenzene nitration experiments conducted in the batch reactor are presented in Table 2.

It is worth emphasizing that the nitration

experiments were carried out for the sole purpose of obtaining the nitrochlorinated mixture that would be used in the alkaline hydrolysis experiments, since the main target of this work was the conversion or the removal of DNCB from the nitrochlorinated mixture.

In the following figures, the graphs on concentration versus reaction time for alkaline hydrolysis in the reactor and in the contactor are presented. In these graphs, DNCB concentration, x , as a function of required reaction time, t , is shown.

Table 2: Experimental data on the MCB nitration reaction

Compound	C (%)	
	1 st reaction	2 nd reaction
Chlorobenzene	17.31	16.04
m-nitrochlorobenzene	0.61	0.63
p-nitrochlorobenzene	51.71	52.80
o-nitrochlorobenzene	29.12	29.69
2,4 dinitrochlorobenzene	0.80	0.56
2,6 dinitrochlorobenzene	0.06	0.05
Others	0.39	0.23

The Effect of Sodium Hydroxide Mass Fraction

Sodium hydroxide mass fraction had a considerable effect on the process, since this reagent was the main agent in the conversion of DNCB into dinitrophenolate. Solutions with 5.0% and 10.0% NaOH mass fraction were tested, using both the glass reactor and the RDC contactor. Time evolution of the NaOH mass fraction is shown in Figures 3 and 4 for the experiments conducted in the reactor and with the RDC, respectively.

As can be observed in Figures 3 and 4, good

results were obtained for the conversion of DNCB into dinitrophenolate, since all curves show the continuous decrease of the DNCB mass fraction. In the experiments conducted in the glass reactor, de DNCB mass fraction showed a slight decrease and stabilized after 0.5 hour had elapsed. In comparing the curves, one can verify that higher rates of conversion of DNCB into dinitrophenolate were attained in the tests with 10.0% NaOH mass fraction solution. This was expected since higher NaOH mass fractions facilitate the kinetic effect, according to Equation 3.

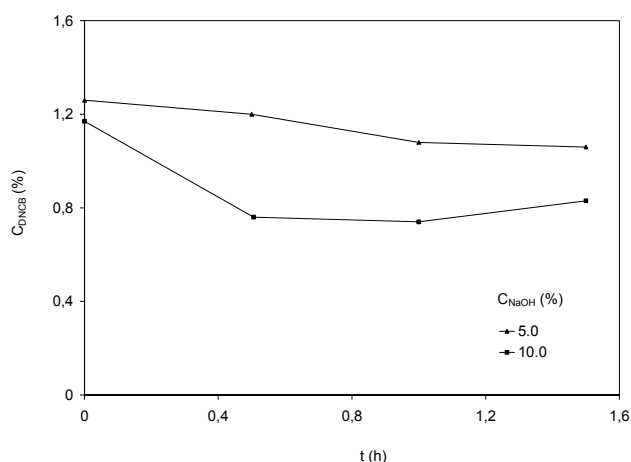


Figure 3: Time variation in the DNCB mass fraction in the nitration reactions.

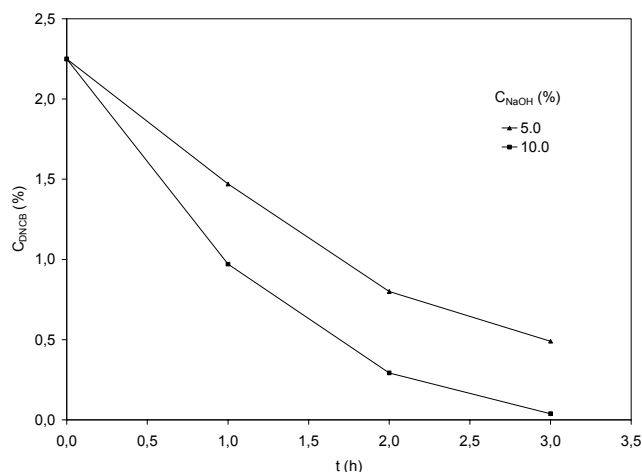


Figure 4: Time variation in the DNCB mass fraction in alkaline hydrolysis reactions ($N=1000$ rpm).

The Effect of RDC Rotation Velocity

The effect of rotating disc velocity on DNCB alkaline hydrolysis was also considered. Experiments were conducted at two different rotation speeds, 1000 and 2000 rpm, using 15.0% and 10.0% initial NaOH mass fraction solutions. The results of the DNCB conversion into dinitrophenolate are presented in Figures 5 and 6 as a function of time.

It can be clearly verified in Figures 5 and 6 that rotation speed directly affects equipment performance independent of the NaOH initial mass fraction. In both figures, it can be observed that lower DNCB mass fractions were obtained with the RDC operating at 2000 rpm than at 1000 rpm. This is due to the fact that higher disc rotation velocities result in better mixing rates and, consequently, better efficiency levels are also obtained.

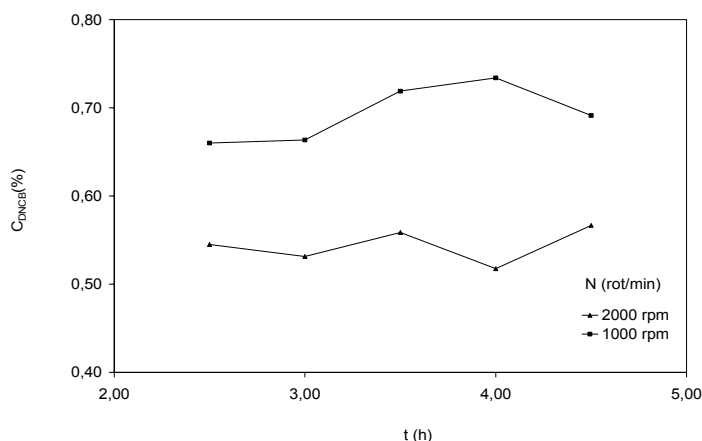


Figure 5: Variation in C_{DNCB} with time in alkaline hydrolysis reactions using the RDC ($C_{\text{NaOH}} = 0.10$).

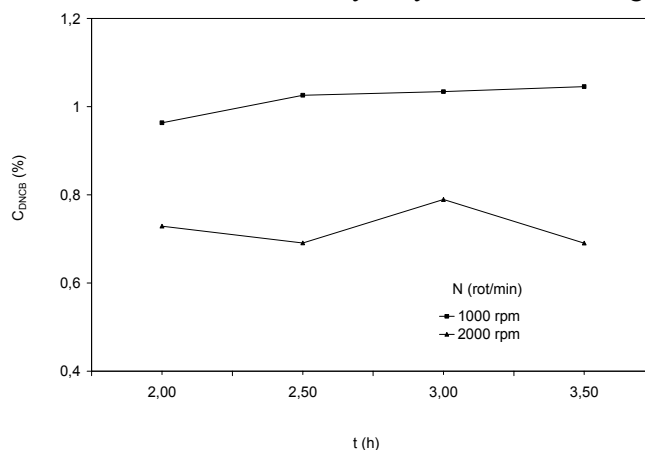


Figure 6: Variation in C_{DNCB} with time in alkaline hydrolysis reactions using the RDC ($C_{\text{NaOH}} = 0.05$).

Comparison of the Performance of the Glass Reactor and the Rotating Disc Contactor (RDC) in Alkaline Hydrolysis

The performance of both pieces of equipment in alkaline hydrolysis was also compared. In these experiments, the initial NaOH mass fraction was the same, 5.0%, for both pieces of equipment. The time evolutions of the DNCB mass fraction in the glass reactor and in the RDC contactor are compared in

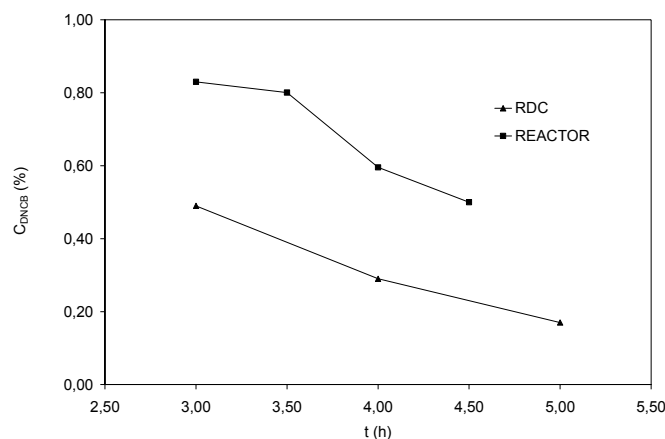


Figure 7: Comparison of time variation in C_{DNCB} in alkaline hydrolysis reactions using the glass reactor and the RDC contactor ($C_{NaOH} = 0.05$).

CONCLUSIONS

The removal of DNCB from industrial residuals by a process of liquid-liquid extraction with chemical reaction was experimentally studied.

A glass reactor and an RDC contactor were used for the conversion of DNCB into sodium dinitrophenolate in nitration and alkaline hydrolysis reactions with NaOH solutions. The influence of sodium hydroxide mass fraction and of RDC rotating disc velocity on DNCB conversion was assessed and the performance of the two different reactors was compared.

The main conclusion reached in the present work is that recovery of DNCB through its conversion into sodium dinitrophenolate using alkaline hydrolysis is clearly possible. It is also concluded that this conversion may be by both continuous and batch processes and that the RDC contactor is a piece of equipment that can perfectly be used in both cases.

Another important conclusion reached regards the range of the RDC operation in these processes. Two disc rotation velocities were tested and it could be verified that for the higher velocity, better conversion rates were obtained.

Figure 7.

It can be observed that the conversion of DNCB into dinitrophenolate was more effective using the reactor than using the RDC contactor. This had been expected, since the mixing level in the reactor was better than that in the contactor. However, the advantage of using continuous processes, as is the case of the RDC contactor, on an industrial scale, rather than batch processes, should be emphasized.

Finally, from the present work it can be deduced that, when the RDC contactor is used, alkaline hydrolysis may be an excellent alternative to industrial processes where removal or recovery of nitrochlorinated aromatic compound residuals is required.

NOMENCLATURE

C	mass fraction,	%
C_{DNCB}	DNCB mass fraction,	%
C_{NaOH}	NaOH mass fraction,	%
N	disc rotation velocity,	rpm
t	time,	h

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