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CATALYTIC BEHAVIOR OF BIOSORBENTS SUPPORTED IN ZEOLITES

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Abstract

The catalytic oxidation of 1,2-dichlorobenzene at 350 ^{o}C was investigated over a robust biosorption system consisting of a bacterial biofilm supported on NaY or NaX zeolites. The batch method has been employed using chromium concentrations in solution ranging from 50 to 250 mg_{Cr}/L. The results showed that the maximum removal efficiency was 20% for Cr in both systems based in NaY or NaX. The bacterial biofilm, *Arthrobacter viscosus,* supported on the zeolite reduces Cr(VI) to Cr(III). The Cr(III) is retained in the zeolite by ion exchange. The new biosorvents catalysts were characterized by spectroscopic methods (FTIR and ICP-AES), surface analysis (DRX) and thermal analysis (TGA). The various techniques of characterization used show that this biosorption process does not modify the morphology and structure of the FAU-zeolites. These catalysts, Cr/FAU, prepared through this new procedure present good activity and selectivity for dichlorobenzene oxidation in wet air. The Cr_{50}-Y was selected as the most active, selective and stable catalyst for oxidation of 1,2 dichlorobenzene in wet air.

Keywords: Zeolites; *Arthrobacter viscosus*; Biosorvents; Cr/FAU; VOCs; Oxidation

1. Introduction

Nowadays, pollution control is one of the major concerns for the scientific community as well as for environmentalists. The major pollutants are the greenhouse gases, metal, organic and inorganic effluents and volatile organic compounds (VOCs). Cadmium (Cd), chromium (Cr) and lead (Pb) are common toxic pollutants in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanneries. The soils are contaminated and pose a risk of metals groundwater and surface water contamination. Numerous processes exist for removing dissolved heavy metals including chemical precipitation, ion exchange, membrane filtration, reverse osmosis and carbon adsorption [1].

Activated carbon adsorption is considered to be a competitive and effective process for the removal of metals at trace quantities. However, the use of activated carbon is expensive for small industries with tight budget and they need alternative technologies or sorbents for these treatments [2-3]. In this regard, zeolites have a great potential for removing heavy metal from industrial wastewater. The existence of a net negative structural charge in the structure promotes a strong affinity for metal cations which give good adsorption properties to these supports. Sodium, potassium and other positively charged exchangeable ions occupy the channels within the three-dimensional structure and can be replaced by heavy metals [4].

The application of natural zeolites to wastewater treatment have been done in recent years. The removal of heavy metals from wastewater using clinoptilolite, the most and abundant zeolite in nature, was studied. The results indicated that the ion exchange loading values could range from 1.6 mg/g for Pb^{2+} to 0 mg/g for Cr^{3+} [5]. One

of the approaches to remove the Cr^{3+} from solution is to combine biosorption by a bacterium with ion exchange capacity of a zeolite.

Biosorption is the accumulation of metals by biological materials without active uptake and can be considered as a collective term for a number of passive accumulation processes which may include ion exchange, coordination, complexation, chelation, adsorption and microprecipitation [6]. Other authors [7] referred that biosorption is the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediation or by purely physico-chemical pathways of uptake.

Bacteria are quite adequate for heavy metals biosorption due to their ability to sorb metal ions, suitability for natural environments and low cost. *Arthrobacter viscosus* is a good exopolysaccharide producer, which, by itself, would allow foreseeing good qualities for support adhesion and for metal ions entrapment [8]. The new systems combine the biosorption properties of the microorganism with some characteristics of the heterogeneous catalysts, such ion exchange properties and shape selectivity.

Among different heavy metals that may be removed from liquid solutions by biosorption, chromium demands special attention as it may present several oxidation states. Chromium was removed from $K_2Cr_2O_7$ liquid solutions with different initial concentrations. A possible reduction of $Cr_2O_7^{2-}$ may be performed by the biofilm itself. The metabolic reduction has been studied and modelled for different pure bacterial cultures [9]. *Arthrobacter viscosus* bacterium supported on the zeolite reduce Cr(VI) to Cr(III) and the Cr(III) is retained in the zeolite by ion exchange.

Catalytic oxidation is one of the most promising technologies for the removal of organic compounds from waste gas (VOCs and POPs). In this context, dichlorobenzene known to be an important precursor of PCDDs and PCDFs was chosen as a suitable model compound for the catalyzed deep oxidation of chlorinated Persistent Organic

Pollutants (POPs). Catalytic oxidation of chlorinated aromatics is generally carried out over three main catalyst types: TiO_2 based V_2O_5/WO_3 [10-16], noble metals (Pt, Pd) supported on various oxides [17-20] and zeolites [21-24]. According to recent studies, zeolites seem to be very promising towards oxidation of chlorinated compounds [25-27]. However, the cost of noble metals justifies their substitution by transition metals. In this case, the proposed solution takes advantage of the synergetic effect between the ability of the biological material, i.e. reducing the metalic ion, and the ion exchange performed by the zeolites.

This work presents the oxidation of 1,2-dichlorobenzene in wet air at 350 ^oC over Cr/FAU. The catalyst samples were prepared from a robust biosorption system consisting of a bacterial biofilm supported on faujasite (FAU) zeolites. The NaY or NaX worked as a support for the biofilm and was mixed with an inoculated medium with *Arthrobacter viscosus* bacterium, in batch experiments. The new biosorbent supported in the zeolite was tested with low concentration of chromium. Total metal cations concentrations were measured with an atomic absorption spectrophotometer. The results showed that the maximum removal efficiency was 20% for Cr in both systems based in NaY or NaX, and the *Arthrobacter viscosus* bacterium supported in zeolite reduces Cr(VI) to Cr(III).

2. Experimental

2.1. Materials and Reagents

Arthrobacter viscosus was obtained from the Spanish Type Culture Collection of the University of Valência. Aqueous chromium solutions were prepared by diluting $K_2Cr_2O_7$ (Aldrich) in distillated water. The faujasite zeolites NaY (Si/Al = 2.88) and

NaX (Si/Al = 1.63) were obtained from W.R. Grace. The zeolites were calcinated at 500 ^{o}C during 8 hours under a dry air stream prior to use.

2.2. Reaction Study

Catalytic activity tests were carried out in a fixed bed reactor (i.d. = 10 mm), under atmospheric pressure and at 350 °C using 0.14 g of catalyst (grain size between 200 and 400 µm). Before reaction, catalyst samples were pretreated in situ under dry airflow (90 $ml.min^{-1}$) at 350 °C for 6 hours, then cooled down to the reaction temperature. 1,2 Dichlorobenzene ($C_6H_4Cl_2$) was introduced into the reactor using a bubbling flask containing $C_6H_4Cl_2$ swept by a dry air flow, leading to a gaseous mixture directed to a condenser maintained at +15.2 °C. The resulting effluent was then mixed with wet air to ensure that hygrometric level was matching industrial conditions. For the standard condition, the reactant mixture contained 1.03% of water (corresponding to an hygrometry of about 50%) and 667 ppm of $C_6H_4Cl_2$. The total gas flow was 75 $ml.min^{-1}$ with a GHSV of 18.000 h^{-1}. The reaction products were analyzed using an on-line gas chromatograph, equipped with a FID detector and a VF-5ms column for the analysis of $C_6H_4Cl_2$ and probable polychlorinated benzenes ($PhCl_3$) and with a TCD detector and a Porapak Q column for CO_2 analysis. The carbon balance, including the amount of carbon deposited on the catalyst at the end of reaction, was always higher than 98%. Mass spectrometer (Thermo Finnigan Automass Multi) and specific Dräger tubes were used to detect the eventual Cl_2 and phosgene production (never observed in this work).

2.3. Preparation of the biofilm supported in zeolites

The preparation of the biosorbents was carried out using the batch method and all experimental work was conducted in triplicate. Batch adsorption experiments were

conducted using 1.0 g of the Y or X zeolites with 150 mL of the different dichromate solutions (50, 100, 150 and 250 mg_{Cr}/L) and 15 mL of *Arthrobacter viscosus* culture media in a 250 mL Erlenmeyer flask. For the microorganism growth a medium with 5 g/L of peptone, 3 g/L of malt extract, 3g/L of yeast extract and 10 g/L of glucose was used, sterilized at 120°C for 20 min. The Erlenmeyer flasks were kept at 28 ºC, with moderate stirring. Samples (1 mL) were taken, centrifuged and analyzed for metals using atomic absorption spectrophotometry (AAS). The biosorption samples have been identified by designation Cr_nzeolites where *n* represents the initial chromium concentration of solution. Samples with *n* = 50 (50 mg_{Cr}/L), 100 (100 mg_{Cr}/L), 150 (150 mg_{Cr}/L) and 250 (250 mg_{Cr}/L) were prepared with both supports. The Cr_n-Y and Cr_n-X were calcinated at 350 °C during 6 hours under a dry air stream before the catalytic reaction in order to remove the organic matter of the *Arthrobacter viscosus* bacterium.

3. Characterization

Total metal cations concentrations used during the biosorption essays were measured using a Varian Spectra AA-400, an Atomic Absorption Spectrophotometer, AAS. Room temperature FTIR spectra of the samples were recorded on a Bomem MB104 spectrometer. The transmission spectra of the powdered samples were obtained using KBr pellets over the range 4000-600 cm^{-1} by averaging 20 scans at a maximum resolution of 4 cm^{-1}. X-ray diffraction patterns were recorded using a Philips Analytical X-Ray model PW1710 BASED diffractometer system. The solids samples were exposed to the Cu Kα radiation at room temperature in a 2θ range between 5 and 70°. Thermogravimetric analyses of samples were carried out using TGA 50 Shimadzu instrument under high purity helium supplied at a constant 50 mL min^{-1} flow rate. All samples were subjected to a 6 °C min^{-1} heating rate and were characterized between 25

and 600 ^{o}C. The elemental chemical analyses (Si, Al, Na and Cr) were performed by University of Minho, Departamento de Ciências da Terra, using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

4. Results and discussion

4.1. Biosorption method

The fixation of chromium by a biofilm of *Arthrobacter viscosus* supported on NaY and NaX zeolites varying the metal concentration from 50 to 250 mg_{Cr}/L is presented in Figure 1. In steady-state conditions no difference between the two supports is detected and the same is observed at higher initial concentrations. The maximum removal efficiency was 20% for chromium in both systems.

Insert figure 1

The removal of chromium in both systems was fast and presented a typical biosorption kinetics, which includes two phases: the first one is associated with the external cell surface, biosorption itself, and the second one is an intra-cellular accumulation/reaction, depending on the cellular metabolism [28]. The relatively low maximum removal efficiency seems to be connected with the lack of affinity between the anionic charge of the metal ion and the anionic charge of the bacteria and with the high ionic radius of the chromium ion. Although, zeolites have high surfaces areas (500-700 m^2g^{-1}), most of this area is internal. These limitations probably reduce the adhesion of the *Arthrobacter viscosus* bacterium to the support.

4.2. Characterisation of new biosorption materials

The molar Si/Al ratio and the percentage of Cr obtained by bulk chemical analysis are presented in Table 1. In both faujasite zeolites, the difference in the Si/Al ratio between NaY to NaX is due to the higher Al content in NaX. The increase of the number of charge-compensating cations or number of Na must be responsible for the amount of chromium in NaX after the biosorption process. A comparison of the Si/Al ratio in both systems after the biosorption method with different chromium concentration stages suggests that these process do not modify the structure of the FAU-zeolites.

Insert Table 1

The number of chromium molecules per unit cell determined from the amount of chromium taken up by the zeolites after biosorption process as function of the chromium solution concentration are presented in Figure 2. The both systems are able to remove lower amounts of chromium and only the samples with 50 mg_{Cr}/L (Cr_{50}-X and Cr_{50}-Y) have the same amount of chromium removed. When the chromium concentration solution increases, the system based on NaX is more efficient in removing chromium from aqueous solution.

Insert Figure 2

The powder X-ray diffraction patterns of NaY or NaX and Cr_n-Y and Cr_n-X were recorded at 2θ values between 5 and 70 ^{o}. The DRX patterns of parents FAU zeolites and the modified zeolites with chromium are very similar. The slight change in the intensity of the bands in Cr/zeolites patterns are in line. These observations indicate that

the framework of the zeolite has not undergone any significant structural change during incorporation of the ion metal i.e. crystallinity of the FAU-zeolite is preserved during the biosorption method and confirm the presence of Cr^{+3} into FAU-zeolite framework. The data obtained by vibrational spectroscopy (FTIR) can provide information on the presence of chromium and on the crystallinity of the supports. In both systems with Y and X zeolites, the spectra of the parent zeolites and modified zeolites are dominated by the strong zeolite bands: broad band at 3700-3300 cm^{-1} is attributed to surface hydroxylic groups and bands corresponding to the lattice vibrations are observed in the spectral region between 1300-450 cm^{-1} [29]. No shift or broadening of these FAU zeolites vibrations are observed upon inclusion of the chromium by biosorption method, which provides further evidence that the framework zeolite remains unchanged. The IR spectra of the modified Cr_n-FAU exhibits a band at 1400 cm^{-1} attributed to the presence of organic matter from the *Arthrobacter viscosus* bacterium and a band at 1385 cm^{-1} which is assigned to the presence of chromium after the biosorption method. After the calcination, the absence of a band at 1400 cm^{-1} is evidence for the presence of the *Arthrobacter viscosus*.

Complementary studies using a thermal analysis (TGA) contributed to a better understanding of the effect of the *Arthrobacter viscosus* bacterium and the concentration of Cr^{3+} on the thermal properties of framework zeolite. The TGA curve for the parent zeolites shows a weight loss at 120 ^{o}C which may be attributed to the removal of intrazeolite water. After biosorption process, the weight loss of Y and X zeolites occurs in two major stages in the broad temperature range. The first stage presented a weight loss in the temperature above 130 ^{o}C. This loss is due to removal of intrazeolite water and the second stage of TGA curve, 4.8 to 7.6 % weight loss in the temperature at 320 ^{o}C is observed for Cr_n-X and 4.8 to 3.9 % at 330 ^{o}C for Cr_n-Y which

corresponds to the decomposition of organic matter of the *Arthrobacter viscosus* bacterium when chromium concentration increases. The difference between weight loss and amount of organic matter in both systems is due to the different ratio of Si/Al between the zeolites. In fact, the X-zeolites have an increase in the charge-compensating cations due to higher Na number which promote the efficiency of bacterium adhesion. After calcinations, the TGA curves of Cr_n-FAU are very similar with parent zeolites.

4.3. Catalytic reaction

The catalytic oxidation of 1,2-dichlorobenzene (1,2$PhCl_2$) was carried out at 350 ^oC over Cr_{50}-Y and Cr_{50}-X. This study was achieved over Cr_{50}-FAU because these samples present approximately the same quantity of chromium per unit cell (Fig. 2.). The conversion of 1,2-$PhCl_2$ and into CO_2 were reported in figure 3 as a function of time on stream.

Insert Figure 3

Insert Table 2

Whereas Cr_{50}-Y is stable (table 2), Cr_{50}-X slightly deactivates, global conversion decreases from 60% after 5 minutes reaction to 35.5% after 4h. Residual activity (A_R) taken as the ratio of initial to final conversion is close to 0.6 on Cr_{50}-X catalyst against near 1 over Cr_{50}-Y sample (table 2). Deactivation of Cr_{50}-X catalyst was certainly due, as in the case of dichloromethane degradation [26] to the loss of part of sodium cations, which are substituted by protonic sites. Thus Cr_{50}-Y appears as more active that Cr_{50}-X catalyst (table 2). CO_2 and CO (+HCl) were the main products formed during the reaction, no polychlorinated benzenes ($PhCl_3$) and no Cl_2 were observed. Selectivity towards CO_2 was better over Cr_{50}-Y : near 80% against 67% over Cr_{50}-X catalyst (table

2). This better selectivity CO_2 found over Cr_{50}-Y should be due to the higher Na/Cr molar ratio (120 for Cr_{50}-Y and 215 for Cr_{50}-X). New experiment was carried out over Cr_{100}-X catalyst (Na/Cr = 90), initial conversions were greater but catalyst strongly deactivated mainly during the first 0.5h reaction (table 2). After 4h reaction production of CO_2 is 1.5 times higher than over Cr_{50}-X but selectivity in CO_2 was close to 90%.

4. Conclusion

The results reported in this paper show that a biofilm of *Arthrobacter viscosus* supported on Y and X zeolites is able to remove chromium from dilute solutions and can be applied in wastewater remediation. The reduction of Cr(VI) to Cr(III) is performed by the biofilm itself. This metal is exchanged in the zeolite without damage to the original matrix or loss of its crystallinity. These materials show a good properties for catalytic oxidation of 1,2-dichlorobenzene in wet air. Thus Cr_{50}-Y is stable during 4h reaction and able to convert about 50% of dichlorobenzene.

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Caption of figures

Table 1

Chemical analysis of the zeolite samples

Table 2.

1,2-$PhCl_2$ global conversion and into CO_2, selectivity into CO_2 (S_{CO2}) taken after 5 minutes and 4h reaction at 350°C over Cr_{50}-Y, Cr_{50}-X and Cr_{100}-X catalysts. Residual activity (Ar = initial to final conversion ratio),

Fig. 1. Removal of chromium by a biofilm of *Arthrobacter viscosus* supported on (a) Y and (b) X zeolites for different chromium concentration: (**x**) 250 mg_{Cr}/L, (▲) 150 mg_{Cr}/L, (¦) 100 mg_{Cr}/L and (?) 50 mg_{Cr}/L.

Fig. 2. Evolution of chromium-exchanged zeolites by a biofilm of *Arthrobacter viscosus* supported on (a) Y and (b) X zeolites for different chromium concentration.

Fig. 3. Global conversion of 1,2-dichlorobenzene (•) and into CO_2 (▲) as a function of reaction time over Cr_{50}-X (a) and Cr_{50}-Y(b) (T=350 °C).

Sample	Si/Al	Cr content (wt %)
NaY	2.88	--
Cr_{50}-Y	2.88	0.11
Cr_{100}-Y	2.88	0.14
Cr_{150}-Y	2.88	0.15
Cr_{250}-Y	2.88	0.22
NaX	1.63	--
Cr_{50}-X	1.63	0.08
Cr_{100}-X	1.63	0.19
Cr_{150}-X	1.63	0.23
Cr_{250}-X	1.63	0.46

TABLE 1

Catalysts	1,2-$PhCl_2$ conversion (%)				$A_{R(CO2)}$	S_{CO2}.(%)	
	global		CO_2				
	5 min	4h	5 min	4h		5 min	4h
Cr_{50}-Y	47.5	47	37.5	37	0.99	79	79
Cr_{50}-X	60	35.5	40	23.5	0.59	67	66
Cr_{100}-X	99.5	38.5	93.0	34.5	0.38	93.5	89.5

TABLE 2

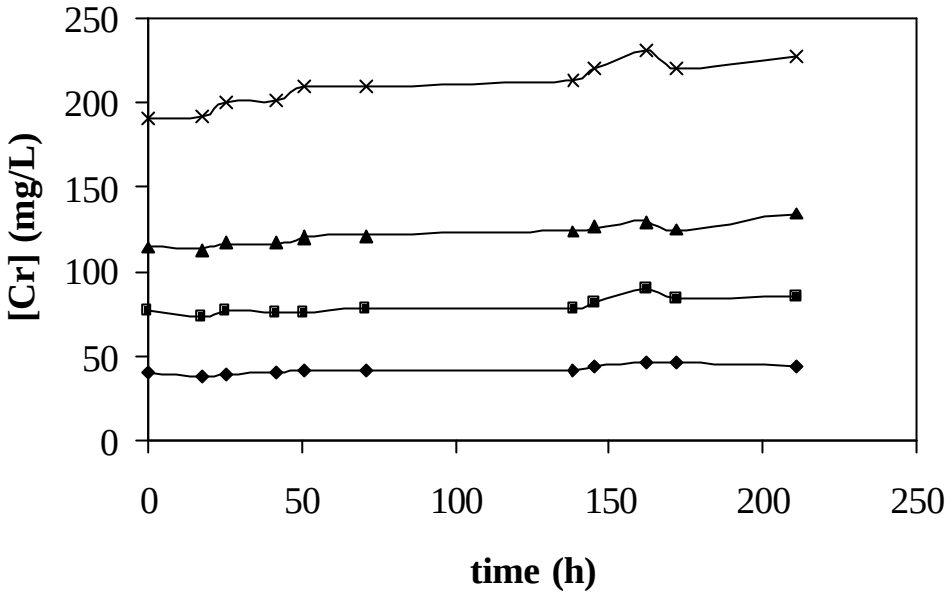

FIGURE 1a

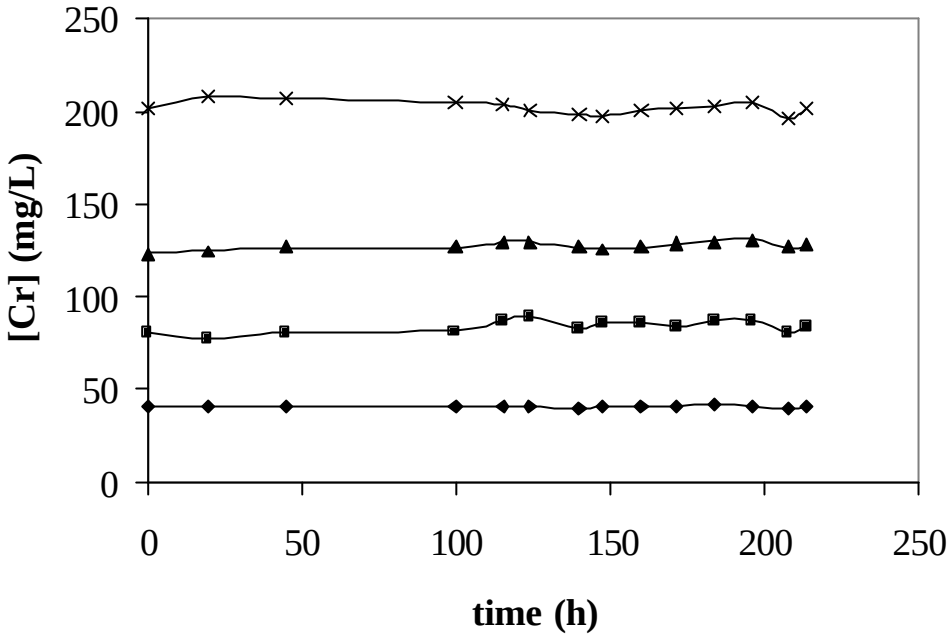

FIGURE 1b

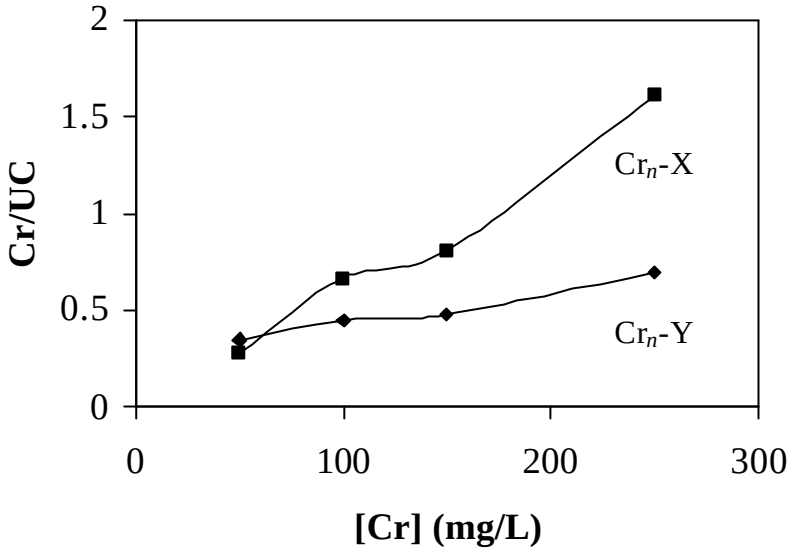

FIGURE 2

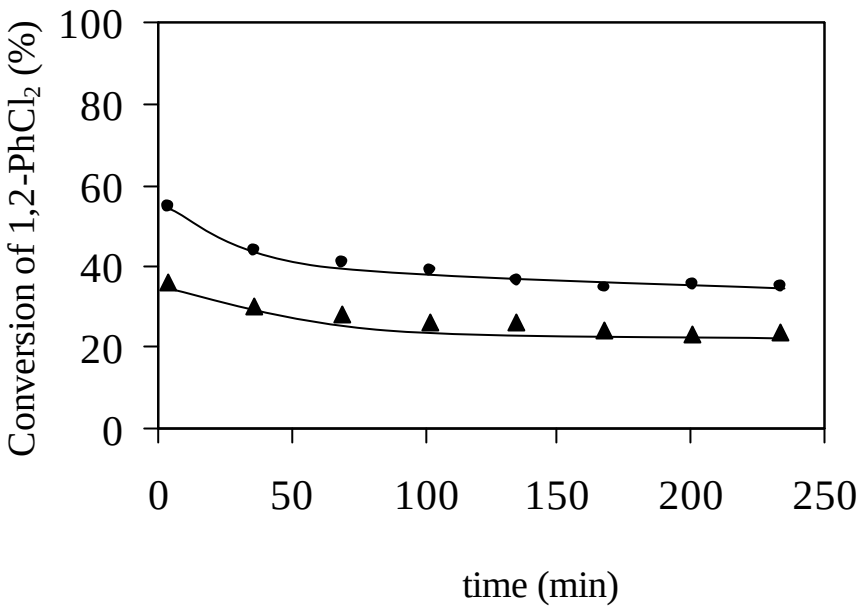
Conversion of 1,2-PhCl2 (%)
100
80
60
40
20
0
0
50
100
150
200
250
time (min)

FIGURE 3a

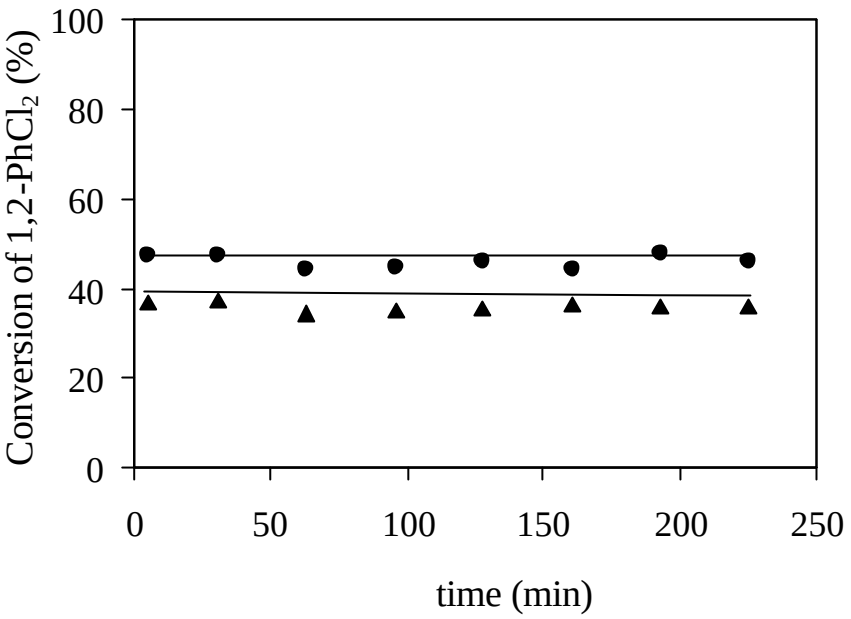
Conversion of 1,2-PhCl2 (%)
100
80
60
40
20
0
0
50
100
150
200
250
time (min)

FIGURE 3b