

**SELECTED PROBLEMS OF PLASTIC WASTE PYROLYSIS
PURIFICATION OF PYROLYTIC OIL FROM CHLORINE
(ORGANOCHLORINE COMPOUNDS)**

Oskar Bartyzel, Tomasz Majka, Krzysztof German

Department of Chemistry and Technology of Polymers,
Cracow University of Technology,
ul. Warszawska 24, 31-155 Kraków, Poland

Abstract

An economical, chemisorption based, method for purification of pyrolytic oil from organochlorine compounds is tested. The experiments with chosen organochlorine have shown, that silver and platinum adsorbents can be used for purification of liquid organic phase. More promising results are found for silver adsorbent. In experiments with dichlorobenzene chlorine level was decreased to 34 ppm Cl in oil at 150 ° C temperature. In experiments with 2-chloroethyl benzoate the chlorine concentration was decreased to 15 ppm Cl level at temperature 220 °C.

Keywords: Plastics pyrolysis, dechlorination, pyrolytic oil, silver, adsorption

Introduction

Present methods of liquid mixture purification from organochlorine compounds based upon reactions with sodium (Na) or calcium (CaO/CaCO₃). These methods are useless for the industry because are either dangerous (Na) or insufficient (CaO/CaCO₃) and produce inorganic waste (both methods). The proposed method bases on reversible chemisorption. Silver and platinum has been investigated as potential adsorbents. The hypothesis originated from the poisoning activity of chlorine for heterogeneous catalysts based upon these metals [1]. Realized experiments have confirmed expected activeness of these metals. Both can be used for purification of liquid organic mixtures from chlorine compounds, but silver is found to be more effective [2]. In this paper we show silver activity for chosen compounds, compare effectiveness difference between silver and platinum supported on Al₂O₃ as well as reveal observed isomerisation reactions.

Experimental Part

The alumina support (γ -Al₂O₃) and alumina-supported catalysts (Pt/Al₂O₃) were obtained from Katalizator Ltd, Kraków. Silver-based adsorbents were

prepared in accordance with [3,4,5]. Silver lactate was used as impregnation salt for silver, due to large of anion of this salt (table 1). Most molecules of chlorinated compounds expected in purified pyrolysis derived oil are large (alkylaromatic) [1], so silver supported in small pores will be unessential for adsorption. Silver lactate was prepared from lactic acid (Fluka AG) and silver sulphate (PPB POCh). Solvent and chlorine compounds: toluene, benzyl chloride, and methyl p-chlorobenzoate were obtained from POCh, Poland, alkyl naphthalene oil (T110) from Nynas Naphthenic AB, decalin, dichlorobenzene and 3-chlorotoluene from Fluka AG. Synthesis of used 2-chloroethyl benzoate is described in [6]. Hydrogen was obtained from Linde Gaz Poland, Ltd.

Table 1. Anion size of chosen silver salts molecule (computed using AM1 procedure).

Silver salt	Name CAS No	Anion size [Å]
$\text{Ag}^+ \left[\begin{array}{c} \text{O} \\ \diagup \text{N} \diagdown \\ \text{O} \end{array} \right]$	nitrate 7761-88-8	2,15
$2 \text{Ag}^+ \left[\begin{array}{c} \text{O} \\ \diagup \text{C} \diagdown \\ \text{O} \end{array} \right]$	carbonate 534-16-7	2,24
$2 \text{Ag}^+ \left[\begin{array}{c} \text{O} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{O} \end{array} \right]$	oxalate 533-51-7	4,27
$\text{Ag}^+ \left[\begin{array}{c} \text{O} \quad \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{OH} \end{array} \right]$	lactate 128-00-7	4,59

The $\gamma\text{-Al}_2\text{O}_3$ support was formed from $\gamma\text{-Al}_2\text{O}_3$ by thermal treatment. Finally, the supported silver ions were reduced to metallic silver with hydrogen. The content of Ag in $\text{Ag}/\text{Al}_2\text{O}_3$ was determined from the weight loss upon reduction of its lactate (about 20 cg/g).

The adsorption experiments were carried out in a three-necked flask equipped with a stirrer, NiCr-NiAl thermocouple and a reflux condenser. The organochlorine compounds were dissolved in alkylated aromatic hydrocarbons (e.g., toluene, alkyl naphthalene oil) and the mixture was kept in contact with the adsorbent (silver or platinum) at the desired temperature. Hydrogen was used for regeneration of the adsorbent. The regeneration experiments were carried out in a pulse micro reactor. After several cycles of adsorption/regeneration, the surface of silver was

regenerated with air. Both regenerations (i.e. with hydrogen or with air) were performed at the temperature of ca. 350 °C.

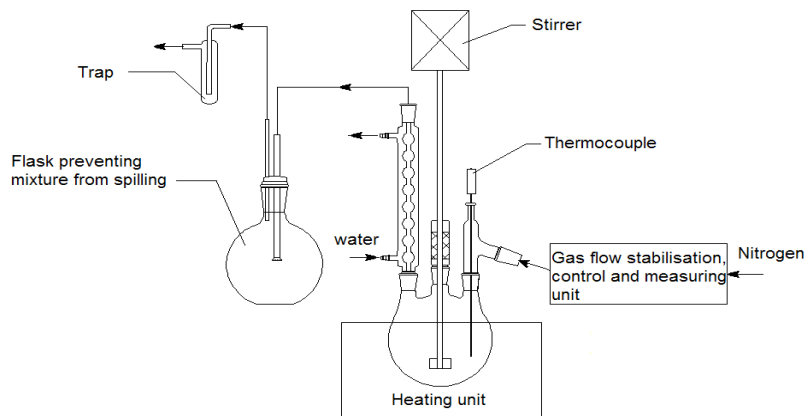


Fig. 1. Schematic of experimental setup for investigations of organochlorine compounds adsorption from liquid organic mixture.

The post experimental mixtures were analysed using gas chromatography (GC coupled with FID detector (Model 8610B, SRI Instruments), equipped with a silica capillary column (RTX-1, 0.53 mm I.D. x 30 mm long) coated with bonded dimethylpolysiloxane phase (0.25 μm thick).

Results and Discussion

Fig. 2 shown adsorption results of 2-chloroethyl benzoate realized at ambient temperature. After 2 weeks more than 90% of chlorine (chlorine compound) has been adsorbed from the liquid mixture. Assuming, that a chlorine atom is being adsorbed on a single atom of silver, then ca 20% of supported silver was active in this experiment. However, if in the process of chlorine adsorption 4 silver atoms take share [7,8] it results in nearly 80% active centres coverage. Besides, adsorption efficiency can also be influenced by spherical effects (in particular the benzoate group size). The new portion of adsorbent added and left in the previously purified oil for next 10 days has adsorbed (Fig. 2) only small amount from the remaining organochlorine compounds, what suggests, that the adsorption equilibrium was reached at this temperature. As a result, silver has adsorbed ca 95 % of chlorine, the remaining chlorine at the end of ambient temperature experiment was 122 ppm Cl.

The adsorption efficiency depends significantly of chlorine atom polarity in organic molecule. Previous experiments (in which benzyl chloride, 3-chlorotoluene and methyl p-chlorobenzoate were dissolved in toluene) have shown, that at 50 °C temperature only benzyl chloride was adsorbed completely.

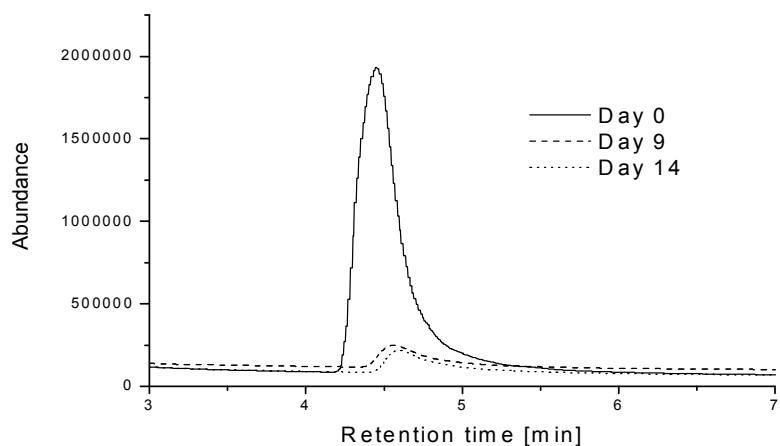


Fig. 2. Cumulated chromatograms of 2-chloroethyl benzoate adsorption from oil T110 on silver in ambient temperature in time (days) function.

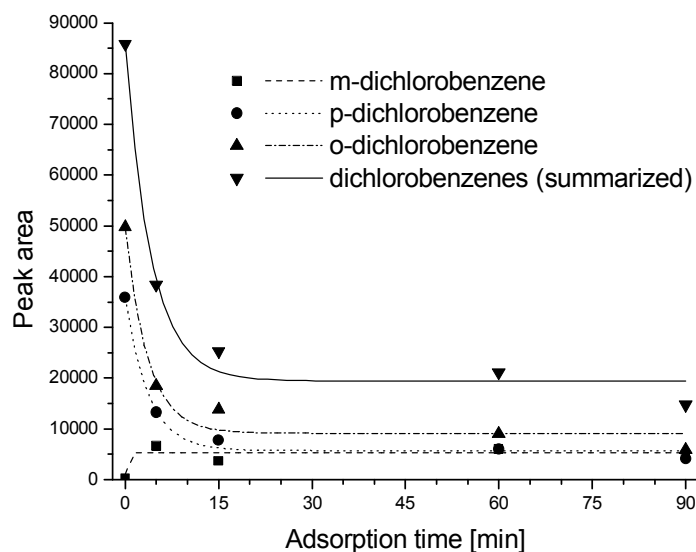


Fig. 3. Adsorption and isomerisation of dichlorobenzene on silver

In the above mentioned molecule chlorine atom is bonded in $-\text{CH}_2\text{Cl}$ group and then negatively polarized. The adsorption efficiency of 3-chlorotoluene (chlorine is bonded to the aromatic ring) was only 40%, even at $100\text{ }^\circ\text{C}$, while at the same temperature methyl p-chlorobenzoate was adsorbed with approximately 70% rate [2].

The next experiment was carried out at temperature 150 °C. The liquid mixture was prepared by dissolving orto- and para- dichlorobrenzenes in T110 oil. Dichlorobenzene was chosen because of 2 chlorine atoms bonded to aromatic ring. When attached in this position, it's polarity becomes positive (unlike in benzyl chloride). The chlorine level in oil was decreased after 120 min from 100 ppm Cl to 34 ppm [2].

During the experiment of o- and p-dichlorobenzene adsorption it has been observed, that the liquid phase has been significantly enriched in meta- isomer. The phenomenon demonstrates, that silver adsorbs and also causes isomerisation of dichlorobenzenes. Fig. 3 presents the proportion change in composition of the isomers mixture during adsorption on silver at temperature 150 °C, measured by GC analysis.

On Fig. 4 are compared adsorption activities of silver and platinum adsorbents. Platinum was chosen because of the properties of Pt catalyst described in [9]. Both experiments were conducted at temperature 150 °C. It can be seen, that at these conditions, silver is a more efficient adsorbent of liquid organochlorine compounds that platinum. The platinum adsorbent can be used however for coarse cleaning of liquid mixtures.

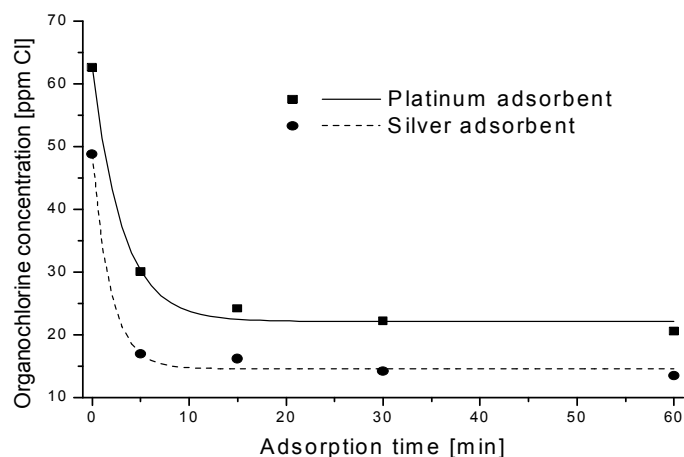


Fig. 4. The comparison of adsorption activity of silver and platinum. Adsorbate: dichlorobenzene. Temperature: 150 °C.

The best adsorption efficiency of the aromatic organochlorine compounds was obtained at 200 - 250 °C with 2-chloroethyl benzoate as organochlorine adsorbed pollutant (Fig. 5).

It is obvious, that silver and platinum can be used in industry only when they can be regenerated. The process, formally a chemical reduction, can be carried out using hydrogen, but also aldehydes [2]. It was also found, that possible residues

on the surface after repeated cycles of adsorption - regeneration can be removed by oxygenation with air at temperatures below 400 °C.

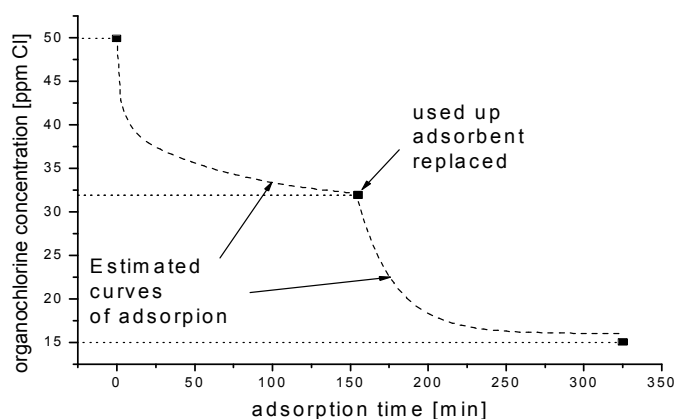


Fig. 5. Two step adsorption of 2-chloroethyl benzoate at 220 °C from T110 oil.

Conclusions

The carried out experiments have confirmed usefulness of silver in purification of liquid organic mixtures from organochlorine compounds. The experimental mixtures are simplified due to technical and analytical limitations in analysis. It can be expected however, that the methods can retain economic also for more complicated liquid systems, such as the pyrolytic oil derived from plastics waste. The proposed purification method requires however further research and conditions optimization in order to use it as a high standard (below 10 ppm) purification process. At the current development state silver adsorbent is applicable for the ambient temperature coarse cleaning. Silver can be regenerated and no new inorganic waste are produced.

References

- [1] German K., Polimery, 55 (5),(2010) 351.
- [2] German K., Pawlikowska E., Kulesza K., Polimery, in press.
- [3] US Patent 4829044, (1989).
- [4] US Patent 4305844, (1981).
- [5] Pinna F.,Catal. Today, 41, (1998) 129.
- [6] Pawlikowska E., Master thesis (pol) University of Technology, Kraków, 2008.
- [7] Fu. H, Jia L., Wang W., Fan K., Surface Science 584 (2005) 187.
- [8] Bovet N., Sayago D.I. at al., Surface Science 600 (2006) 241.
- [9] Windawi H., Wyatt M., Platinum Materials Ref., 37 (4) (1993) 186.