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MICROWAVE REGENERATION OF ACTIVATED CARBON

Microwave radiation, being more and more frequently applied in environmental engineering, is used for regeneration of activated carbon, particularly that saturated with organic substances. This paper is concerned with the use of a microwave field to regenerate a spent activated-carbon-supported catalyst for vinyl acetate synthesis, containing both organic substances and zinc compounds. It has been reported that microwave energy applied directly to a spent catalyst removes some of organic substances from its surface. This results in better leaching of zinc compounds by acid solutions. Compared to repeated leaching performed at boiling points of leach solutions, microwave leaching makes it possible to remove more than 90% of zinc compounds in a shorter period of time, using less energy and smaller amounts of solvents.

1. INTRODUCTION

Microwave radiation is the region of electromagnetic spectrum between 300 MHz and 30 GHz. Microwaves are known to be a quick and energy-saving source of heat. Microwave energy interacting with matter whose dipole moment is stable causes the reorientation of dipoles, and accordingly an increase in the temperature of the whole system. Microwaves are best absorbed by polar substances, particularly water. Hence, microwave application includes drying, quick heating, substance ashing and melting, plasma ashing, mineralization and digestion of organic and inorganic substances as well as extraction and concentration [7], [9], [11].

The literature review shows that in environmental engineering, microwave radiation arouses greater and greater interest [1]–[3], [7]–[12]. Currently, research focuses on:

- the remediation of contaminated soils with organic substances,
- the disposal of medical wastes,
- the disposal of worn tyres,
- the disposal of plastics,
- the regeneration of activated carbon.

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The idea of microwave remediation of granular activated carbon saturated with organic contaminants was initiated by SCHULIN as early as in 1971. DOLANDE et al. [7] and ZHU et al. [12] used a microwave energy to regenerate activated carbon saturated with trichloroethane and hydrogen sulfide. CHA and KONG [1] as well as CHANG YUL CHA and DONG SKI KIM [2] prove that it is possible to employ microwaves to decompose NO_x and SO_2 in combustion product, i.e., gases exhausted to the atmosphere due to incineration. In such a case, activated carbon is not only an adsorbent, but also a body absorbing microwaves. It is also a source of carbon necessary for reducing NO_x . COSS and CHA CHANG YUL [3] propose applying microwaves to regenerate activated carbon saturated with methyl ethyl ketone, acetone and tetrachloroethylene.

Considering the disposal of spent activated carbon, one needs to analyze not only carbon saturated with organic substances, but also carbon containing heavy metals. Spent heterogeneous catalysts used for industrial organic synthesis are a good illustration of this problem [8]. The disposal of spent catalysts containing activated carbon and heavy metal compounds is still a difficult issue. Such catalysts are treated as hazardous waste due to the metal and organic substance content (synthesis by-products). Activated carbon used as a carrier of these catalysts is characterized by a large specific surface area (approx. $1000 \text{ m}^2/\text{g}$), and high mechanical strength. Further research should focus on the regeneration of spent catalysts containing activated carbon and a heavy metal with the aim of reusing activated carbon as a sorbent of environmental contaminants.

In order to regenerate activated carbon-supported catalysts, the remnants of the activated phase including various metals, metal compounds as well as organic substances being by-products of a catalyzed reaction have to be removed from the catalyst surfaces. Since these catalysts contain the substances mentioned and their active phase is bound to a carbon carrier, their chemical regeneration is actually the only method considered here. References [4], [5] discuss the results of regeneration of a spent activated carbon-supported catalyst for vinyl acetate synthesis denoted by C_2 . The catalyst contains zinc acetate, ethyl acetate, basic zinc acetate, zinc oxide, zinc, acetic acid, acetone, ethyl acetate, a small amount of vinyl acetate, acetic aldehyde, croton aldehyde, propion aldehyde, ethylidene diacetate, and their polymerization and polycondensation products. The regeneration described in [4] involved leaching with the 0.1M HCl and 0.1M CH_3COOH solutions. The results of the leaching process conducted for 8 hours at the solutions boiling points were not satisfactory. The efficiency of zinc leaching was low, i.e., 32.41% and 29.52% in the presence of the HCl and CH_3COOH solutions, respectively. The specific surface area of the regenerated activated carbon was small, slightly exceeding $100 \text{ m}^2/\text{g}$. This indicated that the carbon pores contained both remnants of the active phase and also organic substances.

In [5], the analysis focuses on the use of the extraction of CO_2 in a supercritical state to remove organic substances detected on the surface of a spent catalyst, C_2 . The extraction is followed by leaching the active phase remnants, i.e., zinc compounds, by means of a hydrochloric acid solution. The investigation results testify to a high effec-

tiveness of this procedure. The regenerated activated carbon had a specific surface area of $980 \text{ m}^2/\text{g}$, good sorption properties and its iodine number was 720 mg/g [6]. The results show that the regeneration of activated carbon being a carrier of a spent catalyst for vinyl acetate synthesis requires removing first the remnants of organic substances and then the remnants of the active phase.

This work is concerned with the regeneration of a spent catalyst for vinyl acetate synthesis by microwaves as an alternative to supercritical extraction. The method involves removing organic substances and leaching them with solutions of hydrochloric, acetic and nitric(V) acids in the presence of a microwave field.

2. EXPERIMENTAL

The tests were conducted for a fresh catalyst C_1 and a catalyst C_2 used during the production of vinyl acetate. The catalyst C_2 comprised 8.5 per cent by weight of zinc.

2.1. MICROWAVE LEACHING

50 cm^3 of a leach solution ($\text{H}_2\text{O}_{\text{dist}}$, 0.01 M/0.1 M HCl, 0.10 M CH_3COOH or 1.0 M HNO_3) was added to 2 g of the spent catalyst, C_2 , which was exposed to microwave radiation of 2450 MHz. The process was conducted with a Plazmatronika UniClever mineralizer, which, unlike microwave oven-type devices, is equipped with a system of antennas. They focus the whole microwave energy on the sample. As it is possible to control the power of the generator, the energy in portions is precisely supplied to the sample. This prevents the sample from overheating, facilitates the processes of leaching/extraction and makes the decomposition of organic matrix complete. The effect depends on the process parameters.

A review of the research into the leaching conditions shows that applying full generating power in an aquatic environment may result in too rapid heating of the system and immediate release of air from the carbon pores. This is followed by a dramatic rise in pressure and automatic shut-down of the generator. Additionally, if the environment is of the oxidizing type, the carbon matrix decomposes. It has been reported that the optimum heating procedure for the C_2 catalyst takes place in two stages: in the first one, 60% of the generator power is supplied for 5 minutes; in the second stage, 80% of the power is supplied for another 5 minutes. Leaching is repeated three times under the same conditions, each time with a new supply of the leach solution.

2.2. DIRECT ACTION OF MICROWAVE ENERGY ON THE SPENT CATALYST, C_2

The samples of the catalyst C_2 were exposed to microwave energy in a microwave

reactor applying 20% of the generator power. Under such conditions, the reaction system reached a temperature of 448 K after a five-minute heating. Microwave energy was supplied continuously for 10 minutes at the temperature range of 448–453 K. The sample heated for 10 minutes was denoted by C₂-10. Another sample, which was heated for 30 minutes, was denoted by C₂-30. The samples C₂-10 and C₂-30 were subjected to the process of single leaching according to the procedure described above.

2.3. SCANNING PROBE MICROSCOPY

The catalyst surface was examined under an Oxford Instruments EME JEOL JSM-5400 scanning electron microscope equipped with a JSJS 300-Series X-ray mineral analyzer (2000 × magnification).

2.4. ZINC ANALYSIS

Zinc concentration in the solutions was assessed after leaching by conducting MERCK Spectroquant-14832 tests.

3. DISCUSSION OF RESULTS

Figure 1 shows an image of a fresh catalyst, C₁, in which 35–38 per cent by weight of zinc acetate constitute the active phase, and the salt is in the form of coarse crystalline clusters covering the surface of the carbon carrier. Figure 2 presents an image of a spent catalyst. Its surface is covered with an amorphous layer of deactivated substances. The analysis of the catalyst composition shows that the zinc content was approx. 8.5 per cent by weight and the carbon content increased substantially to about 70%.

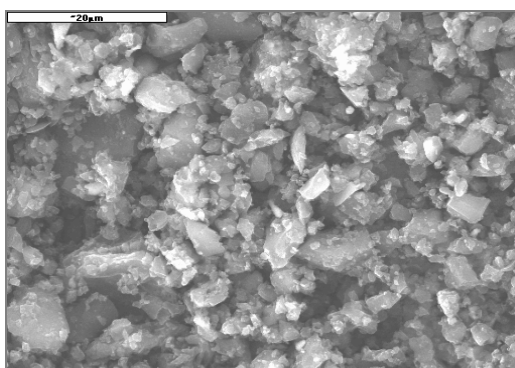


Fig. 1. SEM image of the surface of the fresh catalyst, C₁ (2000 ×)

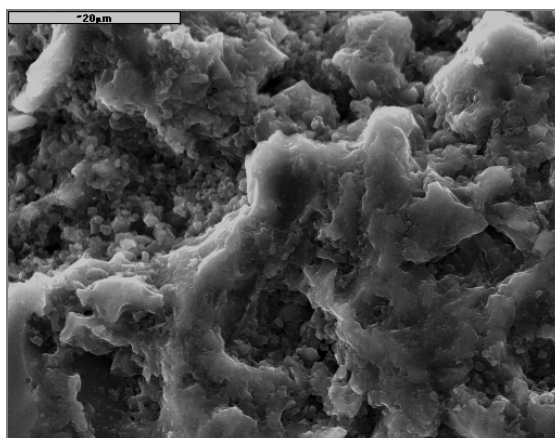


Fig. 2. SEM image of the surface of the spent catalyst, C₂ (2000×)

Considerable changes were observed on the surface of the spent catalyst, C₂, exposed to microwave radiation. The samples were heated for 10 and 30 minutes at a temperature ranging from to 448–453 K, the catalysts being denoted by C₂-10 (figure 3) and C₂-30 (figure 4), respectively. Microwave radiation and heating of the catalyst granules resulted in the vaporization of part of the organic compounds and, therefore, breaking the continuity of the amorphous deposit found on the surface of the spent catalyst, C₂ (figure 2). More changes were observed for C₂-30 than for C₂-10 (figure 4).

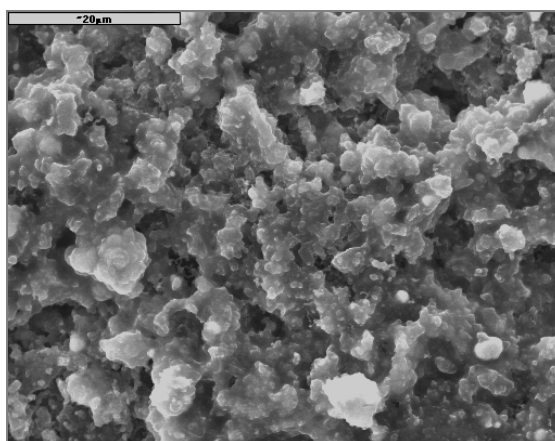


Fig. 3. SEM image of the C₂-10 catalyst surface (2000 ×)

The changes in the surface structure of a spent catalyst occurring as a results of microwave radiation provide evidence of the method effectiveness. Even though the removal of organic substances was only partial, it is assumed that the efficiency of

zinc compound leaching and, consequently, the regeneration of activated carbon as a carrier of the spent catalyst can be enhanced.

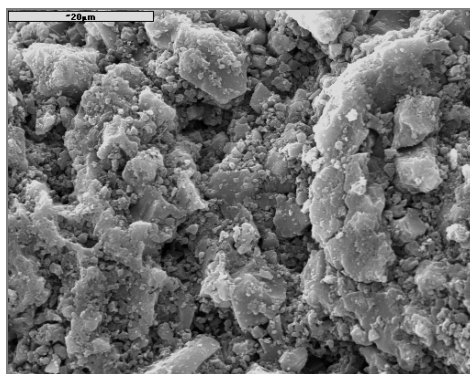


Fig. 4. SEM image of the C₂-30 catalyst surface (2000×)

Then, the behaviour of three catalysts, C₂, C₂-10 and C₂-30, was analyzed. The leaching process was performed with water and acid solutions exposed to microwaves. The results of the leaching process are presented in table 1. One of the solvents used for leaching was distilled water. As a polar solvent with a high dielectric constant, it increases the system temperature and, accordingly, transfers the microwave energy to the solid [9], [11]. Water was reported to be a poor leach solution with respect to the system analyzed, thus the leaching efficiency was influenced by microwave energy and increased pressure acting on the spent catalyst, C₂. The leaching process was conducted at the temperature range of 383–388 K and a pressure of 0.15 MPa. As can be seen from table 1, 28.2% of the zinc compounds were removed. Compared to conventional leaching conducted as direct heating at the boiling point of the solution applied [4], the microwave leaching process lasts shorter and requires a considerably smaller amount of the regenerating agent.

Table 1

Efficiency of zinc removal from a spent catalyst, C₂, in the process of triple leaching with selected solutions using microwave energy

Leach solution	Zinc removal efficiency (%)		
	Leaching I	Leaching II	Leaching III
H ₂ O	11.8	22.5	28.2
0.01 M HCl	25.4	27.6	28.4
0.10 M HCl	32.1	35.6	39.2
0.10 M CH ₃ COOH	17.1	28.4	32.4

Like in [4], activated carbon from the spent catalyst, C₂ is regenerated by the solutions of hydrochloric and acetic acids. The method discussed in this paper requires

microwave energy as an agent increasing the heating time and improving its economy. Microwaves are found to be an important factor; they allow the zinc compounds to be removed more effectively than during classic heating described in [4]. Under the predetermined conditions, the regeneration system had a temperature of 385–392 K and a pressure of 0.15 MPa, which resulted in the removal of approx. 39% of zinc with the 0.1M HCl solution and 32% of zinc with the 0.10M CH₃COOH solution in a much shorter period of time (30 minutes instead of 8 hours) using smaller amounts of leach solutions (150 cm³ compared to 1600 cm³ in traditional leaching [4]).

Table 2 shows the removal of zinc compound from the C₂-10 and C₂-30 catalysts exposed to a microwave field. As predicted, the “disturbance” of the structure of organic substances found on the catalyst surface resulted in highly effective leaching of zinc. Even single leaching under such conditions seems to improve the efficiency of zinc removal. When applying 0.1 M HCl, it is possible to increase the leaching efficiency to 76.1%. The most effective removal of zinc compounds was achieved by applying the 1.0 M HNO₃ solution. The efficiency of zinc removal from the C₂-10 catalyst was as high as 56.4%, whereas for the C₂-30, this efficiency reached 92.7%. These very good results must be mainly due to a microwave field in a heating stage when the part of organic compounds are removed. Another cause is probably the oxidation of the organic substances in the environment of nitric(V) acid under the predetermined conditions, which facilitates the compounds melting and migration into the liquid phase. Further research is being carried out to evaluate the sorption efficiency and, therefore, the reuse of regenerated activated carbon.

Table 2

The efficiency of zinc removal from the spent catalyst, C₂, by applying microwave energy directly on the catalyst, followed by its leaching with selected solutions using microwaves

Leach solution	Zinc removal efficiency (%)	
	C ₂ -10	C ₂ -30
H ₂ O	12.5	13.1
0.01M HCl	42.0	50.2
0.10M HCl	50.6	76.1
0.10M CH ₃ COOH	26.6	36.7
1.0M HNO ₃	56.4	92.7

4. CONCLUSIONS

From the study into the regeneration of activated carbon from a spent vinyl acetate catalyst the following conclusions can be drawn:

- A direct exposure of a spent catalyst to microwave radiation causes considerable changes in its superficial structure at the temperatures as low as 448–453 K. Organic substances are partly removed, which enhances the removal of the other substances remaining in an active phase.

- Among the leach solutions used for removing zinc compounds from the catalyst surface, the most effective was HNO₃ (1.0 M), characterized by good oxidizing properties useful in the removal of organic substances.

- Microwave leaching is a more effective method than a repeated leaching performed at boiling points of the solvents used; zinc compounds can be removed at a lower temperature in a shorter period of time using smaller amounts of leach solutions.

- Microwave energy is reported to be suitable for the regeneration of activated carbon; however, further research in this field is required.

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ZASTOSOWANIE ENERGII MIKROFAL DO REGENERACJI WĘGLI AKTYWNYCH

Energia mikrofal znajduje obecnie coraz szersze zastosowanie w licznych dziedzinach inżynierii środowiska, w tym również do regeneracji węgla aktywnych, głównie nasyconych substancjami organicznymi. W prezentowanej pracy wykorzystano pole mikrofal do regeneracji węgla aktywnego będącego nośnikiem zużytego katalizatora syntezy octanu winylu, w skład którego wchodzi zarówno substancji organiczne, jak i związki cynku. Wykazano, że w wyniku bezpośredniego działania mikrofal na zużyty katalizator z jego powierzchni zostaje usunięta część substancji organicznych, co istotnie ułatwia wyługowanie związków cynku roztworami kwasów. W tych warunkach, wykorzystując ogrzewanie mikrofalowe na etapie ługowania, usunięto z powierzchni zużytego katalizatora ponad 90% związków cynku w krótszym czasie i przy mniejszym zużyciu energii i rozpuszczalników niż podczas wielokrotnego ługowania w temperaturze wrzenia roztworów.