

HEATING AND REGENERATION IN MICROWAVE OF THE ADSORBENT MATERIALS USED FOR NEUTRALIZATION OF CRUDE OIL AND OIL STAINS

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ABSTRACT: Microwave heating has unique advantages over convectional heating methods, including rapid heating and the selective heating of objects. This work has studied two applications of microwave heating in the field of the environment: regeneration of adsorbent materials and activation of adsorbent materials used together with different grains of sand in order to neutralize the stains from crude oil and oil. Thermal behavior during microwave heating of the adsorbent materials used in the experiments,when are dried or saturated with the selected adsorbents has been studied to evaluate the potential for using microwave heating for adsorbent regeneration. Powerful adsorbents of crude oil and various oils in microwaves showed a higher heating rate when were dried. The adsorbents with absorption in microwaves, with low absorbtion, showed faster heating speeds when where saturated with polar components. The short activation time and process simplicity demonstrate that microwave activation of adsorbent materials is a promising approach for turning them into materials with a high crude oil and oils adsorption capacity.
KEY WORDS: granular active carbon; microwave absorption; microwave transparent material.
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1. INTRODUCTION

Microwave heating has been used in many areas due to its unique advantages, the dielectric properties of materials, mostly determines efficiency transfer of the high frequency electromagnetic field into heat form. Therefore, some materials can be quickly heated with microwaves, while others can not be heated at all. An obvious example is that food can be easily cooked in a microwave oven while the plate is still cold. This type of selective heating can greatly improve the energy efficiency of heating objects that strongly absorb the electromagnetic field. The experiments carried out in this paper sought to highlight viable microwave heating solutions in the field of environmental protection, like the adsorbent regeneration and microwave activation of adsorbent materials to transform them into materials with a high absorption capacity of crude oil and various oils.

The emissions of organic vapors, such as volatile organic compounds, are a significant air pollution problem, so the absorption is an effective way of controlling these emissions. Regeneration of the adsorbents requires an ingenious method, so as the usual method for regenerating of adsorbent material is the absorption at temperature, which will lead to waste of energy through the heating of auxiliary parts. Microwave heating is selective due to the difference in the efficiency of absorption of the high frequency electromagnetic field between materials.

The difference between the absorption of microwaves between the adsorbent and the absorbed compound can enable the selective regeneration and energy efficiency of microwaves. For example, a microwave transparent adsorbent can be quickly heated by means of the high frequency electromagnetic field when it is saturated with a polar compound. However, while this compound is desorbed from the adsorbent, the adsorbent absorbs less microwave energy.

Therefore, the thermal behavior of the adsorbents with or without adsorbent in the microwave oven is important for regenerating the adsorbent. Better selectivity of adsorbents and higher energy efficiency can be achieved if the thermal behavior of various adsorbents and adsorbed during microwave heating determines the acceleration of the adsorption process and implicitly the increase of the process yield.

2. EXPERIMENTS AND RESULTS

Adsorption (strict physical adsorption) is defined as enrichment (ie positive adsorption or simply adsorption) or depletion (ie negative adsorption) of one or more components into a surface layer, so as the the adsorption can be grouped into physical adsorption and chemical adsorption [1]. Typically, the adsorbent has a porous structure so that it can have a large surface area, for example, the surface is reported between 900-1100 m2 / g for granular carbon and about 900-100 m2 / g for zeolite [2]. In the physical adsorption, the adsorbate is attached to the surface of the adsorbent by weak physical forces, such as van de Waals force or hydrogen bonds. The adsorption energy does not usually exceed 80kJ / mol. Adsorption may also result in a surface complex, a much stronger physical bond with heats of adsorption up to about 600 kJ / mol for C-N and 800 kJ / mol for chemical bonds. A chemical bond involves sharing electrons between the adsorbate and the absorbent and can be considered as the formation of a surface compound. Because of bond strength, chemical adsorption is difficult to reverse [3].

The adsorption capacity of a particular adsorbent is related to its physical structure, pore size and volume, specific surface area and surface chemistry. The physical absorption of liquids increases with increasing temperature and pressure. The adsorption isotherms give a measure of the adsorption amount (usually the standard volume Va or the molar quantity n) as a function of the partial pressure P / P_0 of the adsorbed at a given temperature. Generally, the most commonly used adsorbent for air and water treatment is active carbon, a high carbon material, high porosity and a high surface area with a high adsorption capacity. Granular active carbon is widely used due to its large porous surface, controllable pores structure, thermal stability, low acid / base reactivity and reduced cost.

The type of application of activated carbon depends on its physical and chemical properties, including pore structure, surface area, ash content and surface chemistry. The Porous from the granular activated carbon have complicated shapes (slots, cylinder, sphere and glass form) with different dimensions, which differ in the shape and size of the usual pores [4].

The ash content refers to the mineral content in the granular active carbon, which derives from the mineral content of the precursor material. Mineral matter can either have a positive or negative effect during activation because it can reduce the activation rate by blocking the carbon zones from the activation gases or by accelerating the rate of activation by catalysing carbon conversion reactions [5].

The nature of the precursor, the type of activation (chemical or physical) and the processing conditions are the three main factors that influence the adsorbent properties of the granular active carbon.

Recovery of the adsorbent is used to restore the adsorbent capacity of the absorbent used. Generally, regeneration methods are based on desorption or decomposition of the adsorbate. The first can be achieved by increasing the temperature, reducing the pressure or displacing the adsorbate, while the latter can be achieved by thermal, chemical or microbiological processes. The regeneration method used is thermal regeneration by steam or in an inert atmosphere [6].

Microwave heating is a new regeneration technique compared to conventional techniques used in industry to regenerate adsorbents. Because microwave energy is volumetric and internal to the heated object, energy consumption can be greatly reduced during microwave heating. Microwave heating is also selective due to the difference in absorption of the microwaves between the materials, depending on their dielectric properties [7]. Generally, non-polar materials have a low dielectric loss factor and poorly absorb microwaves, while polar materials have a high dielectric loss factor and strongly absorb microwaves.

The difference in microwave absorption between the adsorbent and the adsorbed compound may allow the selective and efficient regeneration of the microwave energy of the adsorbent. In the case of adsorbent polar adsorbent and microwave transparent adsorbent, microwave energy will be primarily absorbed by the adsorbent, while the minimum energy will be transferred to the adsorbent. Microwave regeneration has become a promising technology for its ability to achieve both higher energy efficiency and low regeneration costs.

In the paper were used for studies two types of unmodified adsorbents and two modified adsorbents. Unmodified adsorbents consisted of granular activated carbon and silica gel. Modified adsorbents consisted of $AgETS_{10}$ and oxidized granular active carbon [8].

All adsorbent samples were placed in a furnace at a temperature of 150 ° C for an entire day to completely remove any absorbed impurities. A temperature above 150 ° C was avoided, as it could cause the destruction of the structure of some adsorbents, such as the silica gel. A 20 g sample of adsorbent was placed in a 50 ml glass beaker and placed in a microwave oven with adjustable and heated power for a specified period to reach a temperature of 160 ° C as shown in figure 1.

Figure 1. Experimental configuration

Since the output power of the microwave experimental furnace has variable power, it has been run at a "high power" level to ensure that the magnetron working time is the same as the heating time. A temperature sensor was used to measure the temperature without being affected by the high frequency electromagnetic field. The adsorbent temperature was automatically recorded at an acquisition rate of 0.12 seconds [9].

Water, acetone and C_7H_{16} were tested as solvents in these experiments. These solvents cover a wide range of dielectric properties as well as other physical and chemical properties. The dried samples were placed in a vacuum enclosure, each enclosure containing one of these three solvents, where they remained for four days to obtain saturated samples. After adsorption, the temperature profiles of the saturated samples were also measured with the same microwave heating time as the dry adsorbent. Since the maximum temperature of the fiber optic probe is 300 ° C, the microwave oven was switched off when the temperature was close to 290 ° C, even though the heating time was shorter.

Figure 2 shows the temperature profiles of the dried samples during microwave heating. The duration of microwave heating of each sample to reach 160 ° C is indicated in the legend. Since the direction of the heat flow during microwave heating is from the inside to the outside of the heated object, the temperatures at the surface and inside of the adsorbent particles are different. Therefore, it takes time, depending on the thermal conductivity of the adsorbent, before the heat is conducted to the surface of the adsorbent particle where the temperature is measured. In addition, the slow response time of the temperature sensor would further delay measurement of temperature change. Therefore, there is a delay of a few seconds between the temperature measured at the beginning and end of microwave heating.

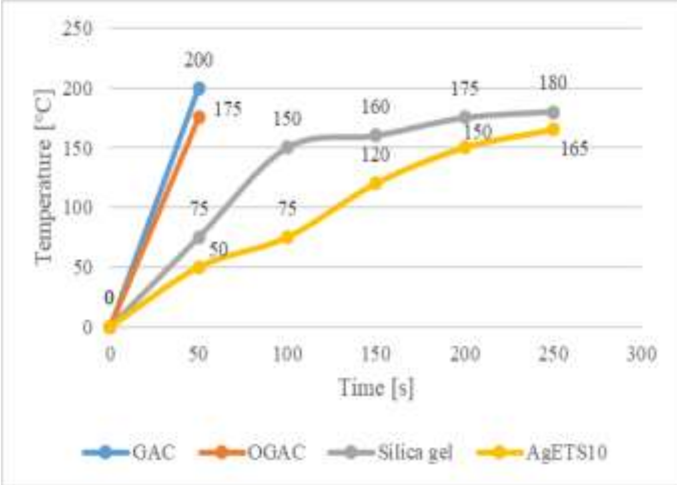

Figure 2. Temperature of samples during microwave heating

Granular active carbon is a highly absorbent microwave material, which is a characteristic of the carbon material due to its semiconductor properties. Both granular activ carbon and oxidized granular active carbon require a shorter duration of microwave heating to reach 160 ° C and have a high heating rate. The maximum heating speed of granular active carbon was 24 ° C / sec (Figure 3) [10]. The other samples are classified from high to low by the ability to absorb the high frequency electromagnetic field: Silicagel and AgETS10. The peak heating rate of $AgETS_{10}$ is 1 ° C / s, the fact that $AgETS_{10}$ has a low heating rate demonstrates that silver can significantly affect the dielectric properties of the materials. From the experiments it was concluded that silver cations become silver metal at high temperatures and modify the dielectric properties of the sample. The heating rate of the silica gel decreases with temperature rise, experimentally it was concluded that such behavior indicates a reduction in dielectric loss with temperature rise. This is why silica gel required more time than $AgETS_{10}$ to reach 160 ° C.

Granular activated carbon samples impregnated with crude oil and oil suspensions tested in this experiments have used particle sizes covering a wide range (from nanometers to micrometers), but most of the particles are very fine. Therefore, the granular active carbon was first ground and then sieved in selected sizes. Three different particle sizes were selected for activation; size 1 (0.2 μm), size 2 (0.6 nm), and size 3 (0.3 mm).

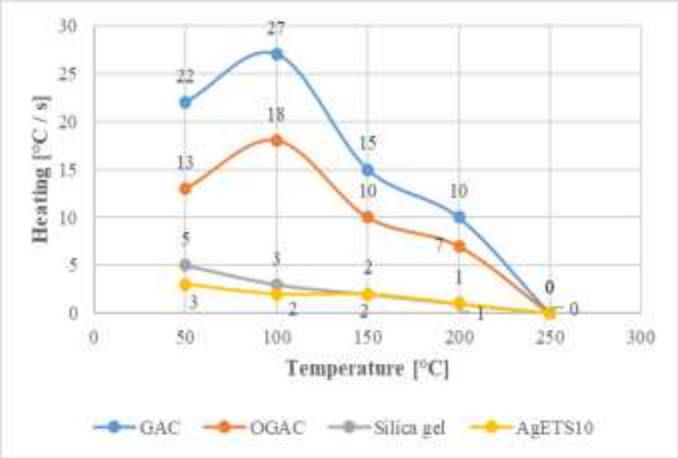

Figure 3. Heating of adsorbents during microwave heating

The setting of the microwave activation of the granular active carbon samples is illustrated in Figure 4, where 20g of a dry granular activated carbon mixture is introduced into a glass container and heated in a high frequency electromagnetic field, the device having adjustable microwave power. The nitrogen gas injected within the amount of 400 cm3 / min passes through the glass container to provide an inert atmosphere.

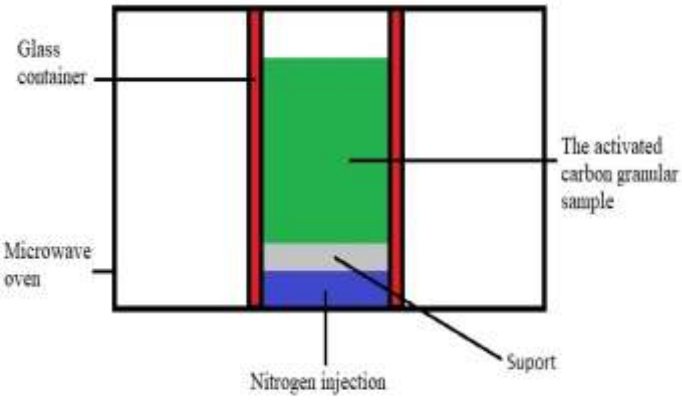

Figure 4. Sample activation furnace diagram

Microwave heating was performed at a frequency of 2.45GHz, with an adjustable power between 0 ÷ 800W. The output power of the microwave oven was controlled by changing the magnetron's operating cycle, each cycle for the microwave generator used in this experiment was 22 seconds. The low level of radiation of this furnace is achieved by feeding the oven in pulses for 8 seconds feeding and switching off for 14 seconds. The relationship between the power level and the operating time of the magnetron is presented in Table 1.

Table 1 - Microwave power according to operating time

	Operation time of the magnetron	
Power	On	Off
High	25	0
Medium	18	7
Low	9	15

3. CONCLUSIONS

Microwave heating is a future method in adsorption applications based on high energy efficiency and heating selectivity. The experiments investigated two applications of microwave heating: regeneration of the adsorbent and preparation of granular active carbon. For the adsorbent regeneration, were selected different adsorbents and solvents to cover a wide range of absorption, the adsorbents consisted of granular activated carbon, silica gel and AgETS10. Solvents included water, heptane and acetone.

The thermal behaviors of dry adsorbents or with solvents have been investigated, from which the following conclusions can be drawn:

- based on the difference in dielectric property between the adsorbent and the absorbed, the microwave heating may be selective to preferentially heat either the adsorbent or the adsorbent;
- among the common adsorbents, the granular carbon is a highly absorbent high-frequency electromagnetic field material, while silica gel is a poorly absorbed microwave material;
- Microwave heating can activate the granular carbon from cude oil and oil stains in a very short period of time, resulting in a high adsorption capacity. For example, in 10 minutes of heating in high frequency electromagnetic field, the activation efficiency is 74%.

4. ACKNOWLEDGEMENTS

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