

Microwave-assisted regeneration of hypercrosslinked polymeric adsorbent saturated with nitrophenols

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Abstract: Thermal regeneration of hypercrosslinked polymeric adsorbent (HPA) was performed at 67°C. Experiments were carried out using a multimode microwave oven operating at 2450 MHz and a thermostatic water bath so as to compare the effect of the different heating mechanisms on the regeneration efficiency of the HPA saturated with nitrophenols. The temperature rise action of the heterogeneous regeneration system under microwave irradiation was described. Additionally, a complete structure and chemical characterization of the regenerated HPA was also carried out in order to study the influence of the subsequent regeneration cycles on the structure and the adsorption capacities of the adsorbents. Structure characterization of the regenerated HPA was accomplished by means of the analysis of FTIR spectra.

Keywords: polymeric adsorbent; microwave irradiation; adsorption; structure

Introduction

Nitrophenols are among the most important phenol derivatives which are widely used as the intermediates of dyestuffs, pesticides, as well as solvents and chemical cleaning agents. They represent an environmental problem because of their toxicity, poor biodegradability and accumulation potential in plant and animal tissues. They may enter into the food chain and have been classified as hazardous pollutants because of their potential to harm human health (Sabio *et al.*, 2004).

Although many different methods have been proposed to remove nitrophenols from wastewaters, using polymeric adsorbent is the most extensive and probably still the most effective way to remove organic contaminants due to adsorbent's high specific surface area, highly developed porous structure, fast adsorption kinetics and relatively small loss in adsorption capacity with each regeneration cycle.

Because of the high cost of polymeric adsorbents, they must be regenerated for reuse after exhaustion. There are many methods used today to regenerate adsorbents. The most extensively used technique is conventional thermal regeneration which involves using heated regeneration solutions to remove organic contaminants and recycle the polymeric adsorbents (Ania *et al.*, 2004). The main problems with this process are long process time (several hours) and the generation of a thermal gradient inside the regeneration system. Microwave heating solves both of these problems by providing both internal and volumetric heating that allow the regeneration to proceed more efficiently at faster heating rate and better distributed bulk temperature (Dieter, 2003). This results in energy saving and shortening of the

process time.

In this work, a comparative study of the regeneration of hypercrosslinked polymeric adsorbent (HPA) using conventional heating method and microwave heating method was performed. To attain this goal, the regeneration of spent HPA was carried out in a thermostatic water bath and in a microwave-assisted heating device under similar operation conditions. The HPA was saturated with nitrophenols in a static adsorption process. The temperature of the heterogeneous regeneration system under microwave irradiation was measured by thermocouple and the temperature rise action was explained. Additionally, a complete structure and chemical characterization of the regenerated HPA was also carried out in order to study the influence of the subsequent regeneration cycles on the structure and the adsorptive capacities of the adsorbents. Structure characterization of the regenerated HPA was carried out by means of the analysis of FTIR spectra.

1 Experimental

1.1 Materials

Hypercrosslinked polymeric adsorbent NDA-150 is a commercial product obtained from Nange Environmental Technology Co., Ltd, Jiangsu Province, China. It can be prepared by the post-crosslinking of porous crosslinked polystyrene in accordance to the Friedel-Crafts reaction in a highly swollen state. The copolymer is characterized by the networks with the crosslinked degree of 40% or even higher, and classified as a separate class of "hypercrosslinked" copolymers. It differs from the conventional St-DVB adsorbents because of its high homogeneity, high inner surface area and high mechanical strength. It pretty much outperforms

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St-DVB based polymeric adsorbents regarding the adsorption capacity with respect to organic compounds.

NDA-150 was used as adsorbent in this work. Prior to the use, the adsorbent was reflux extracted with absolute alcohol for 2 h and washed with 4% aqueous HCl and NaOH solution alternatively twice, then washed with distilled water. After that it was dried at 100°C until constant weight was reached and stored in a desiccator before being used.

The nitrophenols used as adsorbate in this work were *o*-nitrophenol and *p*-nitrophenol. All the compounds were of A.R. grade.

1.2 Methods

A static adsorption process was used as the evaluation of the adsorptive capacity of contaminants. This process was performed as follows: 4.20 g of NDA-150 adsorbent was introduced in a 250-ml flask bottle. Then 100 ml of aqueous solution of *o*-nitrophenol (or *p*-nitrophenol) with known concentration was added to each flask. The flasks were then shaken (100 r/min) in a shaker at 30°C for 24 h. Once saturation has been reached, the suspension in the flask was filtered. Next the saturated adsorbent was washed with distilled water for 2 h, and dried overnight in an oven at 100°C. And the cooled saturated adsorbent was stored in a desiccator and ready to regenerate. The residual concentration of *o*-nitrophenol (or *p*-nitrophenol) in the solution was measured (as described below) to determine the removal efficiency of nitrophenols by the adsorption and the adsorbed amount in the adsorbent. All the experiments were done with an initial concentration of 100 mg/L of *o*-nitrophenol and 525 mg/L of *p*-nitrophenol, respectively. The initial concentration C_0 and residual concentration C_e were measured by a UV-Vis spectrophotometer at the corresponding maximum wavelength. The removal efficiency of *o*-nitrophenol (or *p*-nitrophenol) in the solution was calculated according to the following equation:

$$\eta = \left(1 - \frac{C_e}{C_0}\right) \times 100\% \quad (1)$$

where C_0 and C_e are the initial and equilibrium liquid phase concentration (mg/L) respectively.

The regeneration of the saturated adsorbent was carried out in a thermostatic water bath and in a multimode microwave device, respectively. For the water bath method, the flask filled with the saturated adsorbent was placed in the thermostatic water bath, and then 30 ml of aqueous solution of NaOH with known concentration was added. The water bath was preheated and maintained at the temperature of the regeneration. After the regeneration was performed as required, the suspension in the flask was filtered and the concentration of *o*-nitrophenol (or *p*-nitrophenol)

in the regeneration solution was measured as mentioned above. And then the above process was repeated using 30 ml of water instead of NaOH solution.

The experimental setup for the microwave heating of the adsorbent regeneration is shown in Fig.1.

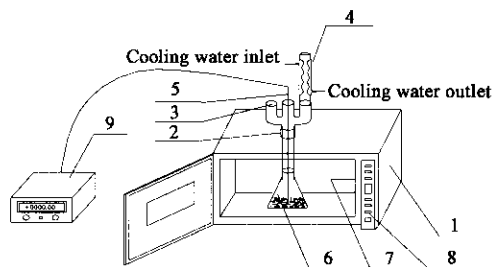


Fig.1 Experimental equipment for the microwave regeneration of the polymeric adsorbent

1. a multimode rectangle cavity; 2. T-joint pipe; 3. feeding inlet; 4. condenser; 5. thermocouple; 6. reactor; 7. microwave inlet; 8. controlling board; 9. temperature regulating and recording apparatus

An 850 W generator working at the frequency of 2450 MHz was used. The flask filled with the saturated adsorbent and 30 ml of aqueous solution of sodium hydroxide with known concentration or distilled water was placed in a multimode cavity where it was exposed to microwave heating. The irradiation time was determined as required. A thermoelectric thermometer was used to measure and to control the temperature of the regeneration system during the regeneration process in order to prevent the adsorbent from overheating. The other operations in this process were the same as the ones in the regeneration process carried out in the thermostatic water bath.

2 Results and discussion

2.1 Effect of microwave irradiation on temperature rise rate of the regeneration system

Temperature is one of the main factors which influence the regeneration efficiency of NDA-150 adsorbent. Microwave radiation penetrates the adsorbent and heats water and other substances in it, and the regeneration efficiency depends on the dielectric and physico-chemical properties of those substances included in the regeneration system. Here the heat was generated by the partial dissipation of the electromagnetic field energy. The alternating electromagnetic field induced the rotation of the dipoles of water and other polar substances present in the adsorbent. The intermolecular friction resulted in the generation of substantial amounts of heat. The heating intensity was the greatest in the case of polar substances, and the most typical representative of

which is water (Raymond, 2000). The absorption capacity to microwave of any substance can be expressed by loss tangent of the substance (Zhou *et al.*, 2003; Jin, 1999):

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (2)$$

where $\tan \delta$ is the loss tangent (-), ε'' is the dielectric dissipation factor (-), ε' is the relative dielectric constant (-).

The $\tan \delta$ values of the essential matters in the experiment are shown in Table 1.

Table 1 The $\tan \delta$ values of the essential substances in the experiment (Jin, 1999)

Name	Measurement temperature, °C	$\tan \delta \times 10^4$	Remarks
Water	25	1570.0	Solvent of regeneration agent
Polystyrene	25	3.3	Essential component of NDA-150 adsorbent
Borax glass	25	10.6	Essential component of the flask

Note: * Measured in 3000 MHz

It can be observed from Table 1 that the loss tangent of water is far larger than that of the other two substances. This indicates that water has the strongest microwave absorption capacity, while the adsorbent and glass are transparent to microwave and can only absorb a little microwave energy. Therefore the temperature rise of the regeneration system in the experiment was mainly caused by the dielectric loss of water in the electromagnetic field. This also shows that microwave heating has selectivity on the substances to heat.

We found that if starting with the initial temperature 7°C and after being continuous exposed to microwave heating for 30 s, the temperature of the regeneration system reached 74°C and obvious "sudden boiling" sounds were heard. The longer the irradiation time was, the more frequently the phenomenon occurred. The reason is that in the liquid-solid heterogeneous regeneration system formed by regeneration agent and NDA-150 adsorbent, the microporosity of the adsorbent is high, and the cavity of the adsorbent is filled with liquid that easily absorbs microwave (water is dominant in the liquid). When irradiated, the adsorbent is transparent to microwave but the liquid included in the cavity is quickly heated under microwave irradiation. The accumulated energy in the cavity cannot diffuse out in the form of heat conduction in a short time, and forms some local "hot spots" in the interior of the adsorbent and leads to the formation of pressure difference in and out the adsorbent. When the pressure difference is large enough the liquid in the adsorbent sends out and

produces the phenomenon of "sudden boiling". To avoid the occurrence of the phenomenon, the experiment of an intermittent microwave irradiation to the regeneration system was carried out. The system was first irradiated for 10–15 s and then irradiation was stopped for some time. The above on-and-off cycle was repeated several times. The experimental results showed that the rate of the temperature rise decreased as the initial temperature of the system went up and the system temperature was controlled under 67°C when the initial temperature was below 53°C and there were no "sudden boiling" sounds heard. On the other hand, the regeneration should proceed at a temperature not exceeding 100°C. It is also of particular importance in the case of NDA-150 adsorbent saturated with nitrophenols, where too high a temperature could result in destruction of the adsorbent structure. Under different initial temperatures the effect of microwave irradiation on the rate of temperature rise of the regeneration system are shown in Table 2.

Table 2 shows at the same NaOH concentration the rate of temperature rise of the regeneration system gradually decreased as the initial temperature went up. This fact is corroborated on the basis of the change of the effective dielectric dissipation factor of water (essential component in regeneration solution) in microwave field.

Table 2 Effect of the initial temperature on the rate of temperature rise

NaOH conc., mol/L	Initial temp., °C	Rate of temp. rise, °C/s	NaOH conc., mol/L	Initial temp., °C	Rate of temp. rise, °C/s
0.1	8	1.93	0.4	7	2.00
	32	1.53		39	1.89
	45	1.45		43	1.60
	53	1.40		49	1.30
0.2	7	1.93	0.5	9	2.30
	32	1.67		33	1.93
	48	1.60		44	1.70
	52	1.47		46	1.20

The rate of temperature rise of water in microwave field can be expressed by the following equation (Wang *et al.*, 2003):

$$\frac{T-T_0}{t} = \frac{\omega \times \varepsilon_0 \times \varepsilon''_{\text{eff}} \times E^2}{\rho \times C_p} \quad (3)$$

where T_0 is the initial temperature (°C), T is the final temperature (°C), t is the microwave irradiation time (s), ε_0 is the vacuum dielectric constant (8.854×10^{-14} F/cm), $\varepsilon''_{\text{eff}}$ is the effective dielectric dissipation factor (-), E is the local electric field intensity (V/m). ρ is the density (g/cm^3) and C_p is the specific heat ($\text{J/(g}\cdot\text{K)}$).

Equation (3) shows that the rate of temperature rise of water is in direct proportion to the effective dielectric dissipation factor of water. Water is a polar compound and has a permanent dipole moment. The effective dielectric dissipation of water in microwave field is mainly caused by the rotation and interfacial polarization of water molecules. On the induction of additional electric field, water molecules are acted by moment of force and their electric dipolar moment direction keeps same as the one of the electric field. As the temperature rises the random thermal motions and intermolecular collisions of water molecules disturb the orientation arrangement of molecular dipolar moment in the direction of the electric field.

The higher the temperature was, the lower the probability of the orientation arrangement of molecular dipolar moment in the direction of the electric field and also the smaller the effective dielectric dissipation caused by the rotation polarization of water molecules. This resulted in the decrease of the rate of temperature rise.

2.2 Efficiency comparison of microwave-assisted regeneration and conventional thermal regeneration

Fig.2 shows the regeneration efficiencies of *o*-nitrophenol- and *p*-nitrophenol-adsorbed adsorbents in microwave oven and thermostatic water bath, respectively.

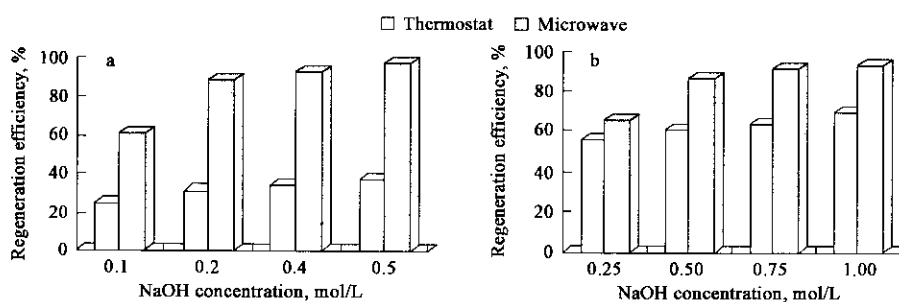


Fig.2 Regeneration efficiency of *o*-nitrophenol (a) and *p*-nitrophenol (b) adsorbed on the NDA-150 adsorbents in thermostat and microwave

In the experiment conventional heating regeneration was carried out in a thermostatic water bath for 1 h at 67°C, and microwave-assisted regeneration was carried out in a multimode domestic microwave oven under an intermittent microwave irradiation. In the process of microwave-assisted regeneration, the saturated adsorbent was exposed to microwave heating once every 5 min. Each irradiation took 10–15 s. The total regeneration time was also about 1 h and the temperature was below 67°C. It is evident from Fig.2 that under the conditions of the same regeneration time and NaOH concentration, the regeneration efficiency of NDA-150 adsorbent saturated with nitrophenols in microwave field is higher than that in conventional heating device, and the difference of regeneration efficiency of *o*-nitrophenol-adsorbed adsorbent is very distinct. This phenomenon may be attributed to the difference on *o*-nitrophenol and *p*-nitrophenol chemical structures. In *o*-nitrophenol molecule the hydrogen bond is formed between nitro group and hydroxyl group. The *o*-nitrophenol adsorption on the adsorbent is mainly caused by the van der Waals force between them. When conventional thermal regeneration is carried out using NaOH solution as regeneration agent, a large amount of sodium *o*-nitrophenol that is water-solubility cannot be formed because there is a chelating ring caused by the hydrogen bond in the *o*-nitrophenol molecule and this results in the lower

regeneration efficiency of the saturated adsorbent when conventional thermal regeneration is performed. For microwave-assisted regeneration of the saturated adsorbent, induced polarization is produced and induced dipolar moment is formed in the *o*-nitrophenol molecule (its permanent dipole moment $\mu = 3.10$) in the microwave field. The inductive effect destroys the stability of the chelating ring in the *o*-nitrophenol molecule and results in the formation of a large amount of sodium *o*-nitrophenol that has a high solubility in water. Therefore the regeneration efficiency of the saturated adsorbent in microwave field is obviously higher than in conventional heating method. As for the regeneration of *p*-nitrophenol-adsorbed adsorbent, the regeneration efficiency under microwave irradiation is higher than in thermostatic water bath, but the difference is not as obvious as the one in the case of *o*-nitrophenol. This may have something to do with the chemical structure of *p*-nitrophenol molecule. In *p*-nitrophenol molecule the nitro group and hydroxyl group are in opposition to each other, and hydrogen bonds can be formed only among *p*-nitrophenol molecules or between *p*-nitrophenol molecule and water molecule, the strength of the hydrogen bonds is weaker, so a large amount of sodium *p*-nitrophenol that is dissoluble in water may be produced whether under microwave irradiation or in thermostatic water bath. The regeneration efficiency of the saturated adsorbent in

both conditions is high.

On the other hand, nitrophenols are compounds easy to be oxidized in the present of oxidizers or in air, especially in alkali circumstances. Therefore in this experiment it is critical to control the temperature of the regeneration system and to avoid the contact of nitrophenols in the regeneration solutions with air. It was reported (Zhang and Xin, 1994) that the oxidation of nitrophenol compounds in aqueous solutions of NaOH can be effectively prevented at lower temperature (below 90°C) conditions. By a simple calculation from Table 2, we can tell that the maximum temperature of the regeneration system can be controlled under 67°C by using the method of intermittent microwave irradiation if the initial temperature does not exceed 53°C. Moreover, due to the regeneration process of the adsorbent saturated with *o*-nitrophenol (*p*-nitrophenol) being carried out in aqueous solution of NaOH, the water in the solution plays a role of preventing nitrophenols from contact with air. The regeneration efficiencies of *o*-nitrophenol-adsorbed adsorbent and *p*-nitrophenol-adsorbed adsorbent in microwave field shown in Fig.2 are 97.59% in 0.5 mol/L NaOH solution and 92.00% in 1.0 mol/L NaOH solution, respectively. This illustrates that the oxidation of nitrophenols in the process of microwave-assisted regeneration is prevented effectively.

2.3 Effect of microwave irradiation on adsorption capacity and structure of NDA-150 adsorbent

Table 3 shows the equilibrium concentration (C_e) and removal efficiency (η) of *o*-nitrophenol and *p*-nitrophenol adsorption on the adsorbent that is repeatedly regenerated in microwave field. The removal efficiency was calculated according to the Equation (1). Fig.3 presents FTIR spectra of crude NDA-150 adsorbent and selected regenerated NDA-150 adsorbent (after six regeneration cycles) respectively.

Table 3 Effect of microwave irradiation on adsorption capacity of the adsorbent

Regeneration times	<i>o</i> -Nitrophenol		<i>p</i> -Nitrophenol	
	C_e , mg/L	η , %	C_e , mg/L	η , %
0	2.22	97.78	0.56	99.89
1	2.77	97.23	1.16	99.77
2	2.29	97.71	1.30	99.75
3	2.10	97.90	0.56	99.89
4	2.20	97.80	1.87	99.63
5	1.46	98.54	1.76	99.65
6	2.47	97.52	0.56	99.89

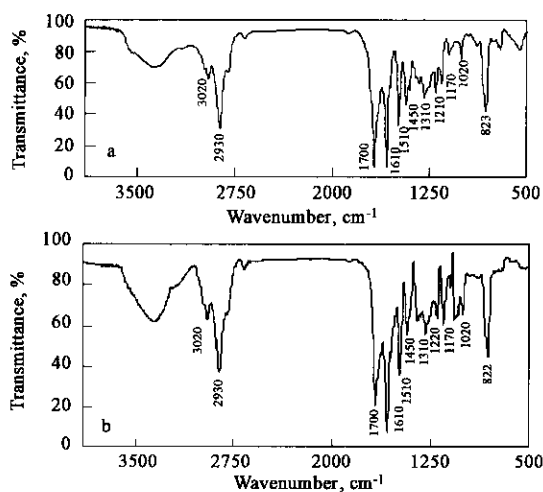


Fig.3 Spectra of crude polymeric adsorbent (a) and regenerated polymeric adsorbent (b)

According to the FTIR spectra, it can be concluded (Shen, 1982) that for the adsorbent there are a strong absorption peak around 1610 cm^{-1} and a weak absorption peak around 1510 cm^{-1} , which are characteristic of benzene ring; there is an absorption peak around 822 (823) cm^{-1} , which shows a contraposition substitution group on the benzene ring; there is an absorption peak around 2930 cm^{-1} , which shows a methylene group on the benzene ring; there are absorption peaks around 1700 and 1310 cm^{-1} respectively, which show a carbonyl group on the benzene ring. The adsorbent has carbonyl group in its structure, and partial polarity of the network would be observed. The FTIR spectra show that the structure of the adsorbent is unchanged before and after the adsorbent being irradiated. This proves that the structure of the adsorbent with the subsequent cycles of microwave regeneration is stable. On the other hand, the experimental results shown in Table 3 indicate that the equilibrium concentration and the removal efficiency of *o*-nitrophenol or *p*-nitrophenol adsorbed on crude and regenerated adsorbents do not have obvious difference. This proves that microwave irradiation does not change the adsorption capacity of NDA-150 adsorbent.

3 Conclusions

One of the main advantages of using microwave energy is that the rate of temperature rise in the regeneration process is high. However, when the regeneration system is exposed to microwave heating for a long time (over 30 s), some local "hot spots" can occur inside the adsorbent. The intermittent microwave irradiation to the system can gradually raise the initial temperatures of the system, and the rate of temperature rise decreases as the initial temperature of the system goes up. When the initial

temperature does not exceed 53°C, the temperature of the system to be exposed to microwave heating can be controlled under 67°C, and some local “hot spots” can be effectively avoided.

Under the conditions of the same regeneration time and NaOH concentration, the regeneration efficiency of the saturated adsorbent is higher in microwave field than in conventional heating device, and the difference of regeneration efficiencies of *o*-nitrophenol-adsorbed adsorbent is distinct. This is due to the formation of the induced polarization in the *o*-nitrophenol molecule in microwave field. The inductive effect destroys the stability of the chelating ring in the *o*-nitrophenol molecule. But the hydrogen bond cannot be formed inside the *p*-nitrophenol molecule, and so the difference of regeneration efficiency of *o*-nitrophenol-adsorbed adsorbent in both regeneration situations is not distinct.

NDA-150 adsorbent has a good property of enduring microwave radiation. The adsorption capacity and the structure of the adsorbent keep unchangeable after the subsequent cycles of microwave regeneration.

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