Characteristics of Ultrasonically Enhanced Low-Temperature Thermal Regeneration of Powdered Activated Carbon: A Case Study of Acetone and Aniline

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Abstract: Effective regeneration of powdered activated carbon (PAC) is the key to reduce the operating cost of the PAC in wastewater treatment processes. In this study, volatile acetone and semi-volatile aniline were selected to investigate the regeneration characteristics of ultrasonically enhanced low-temperature thermal process. The results showed that the regeneration efficiency of the PAC that had adsorbed aniline or acetone increased with the increase in ultrasonic power, and optimal value of frequency and regeneration times were determined. The concentration and properties of organic solvents had a significant influence on the ultrasonic regeneration process. With the increase in heating temperature and regeneration time, the regeneration efficiency increased, but the loss of mass of the saturated PAC increased noticeably. With the combination of ultrasonic treatment in a solvent with low temperature heating, the PAC regeneration efficiency was successfully improved, and the PAC mass loss rate was noticeably reduced. The microjet, shock wave, and cavitation effects produced by ultrasonic treatment restored the specific surface area of the PAC, expanded its mesopore volume, and increased the pore diameter. A reasonable selection of the regeneration solution and optimization of the ultrasonic treatment conditions could create favorable conditions for subsequent low temperature thermal regeneration.

Keywords: powdered activated carbon; low-temperature thermal regeneration; ultrasound; volatile and semi-volatile organic pollutant

1. Introduction

As a broad-spectrum adsorbent, powdered activated carbon (PAC) can adsorb various pollutants in water, such as refractory organic compounds [1], humic acid [2], microbial metabolites [3], and heavy metals [4]. It is widely used for the purification of source water [5], emergency water treatment [6], and advanced treatment of printing–dyeing wastewater [7]. Due to the fact that PAC is a costly material [8], it is usually regenerated and recycled when it is used in a water or wastewater treatment process. In this context, efficient regeneration technologies are required to achieve effective PAC recycling, improve the efficiency of the use of the PAC, and reduce the process operation cost [9].

Currently, methods for the regeneration of activated carbon include biological regeneration [8], thermal regeneration [10–12], ultrasonic regeneration [13–15], solvent regeneration, and advanced oxidation regeneration [16]. The thermal regeneration method is subdivided into low-temperature (105 °C–200 °C) and high-temperature (450 °C–900 °C) methods. The high-temperature thermal regeneration method desorbs, carbonizes, oxidizes, and decomposes the adsorbate by heating is efficient and convenient, but has shortcomings in terms of high energy consumption and great carbon loss [10,11]. The

ultrasonic regeneration method is mainly suitable for the regeneration of the PAC used for physical adsorption, and its primary shortcoming is that its regeneration process is incomplete [15]. When inorganic or organic solvents are used for regeneration (the solvent regeneration method), the loss of the PAC is less. The solvent regeneration method is suitable for reversible adsorption, especially for adsorption of organic matter with a high concentration and a low boiling point [14]. However, the solvent regeneration method has the shortcomings of secondary pollution, incomplete regeneration, and micropore blockage, and the ability to adsorb can decline or be lost after repeated regenerations [10].

The ability to regulate and control the temperature, improve the efficiency, and reduce the carbon loss of thermal regeneration for a variety of potential pollutants is a crucial technical issue in the development of thermal regeneration technologies [10–12]. The low-temperature thermal regeneration process is suitable for the regeneration of the PAC used for physical adsorption, and has a good regeneration effect on PAC that has adsorbed aromatic compounds, lipids, and other compounds with low boiling points [14]. The temperature used in low-temperature thermal regeneration leads to quite different degrees of desorption for different pollutants. For some pollutants, the regeneration cycle has little influence on the regeneration efficiency above a certain regeneration temperature. Shah et al. [11] regenerated saturated granular active carbon that had adsorbed volatile organic compounds (acetone and butanone), and found that when the regeneration temperature was 80 °C, the regeneration efficiency of acetone-adsorbed PAC after the first regeneration reached 95%, and the regeneration efficiency remained unchanged after eight cycles of regeneration. However, the adsorption capacity of butanone gradually decreased after several regeneration cycles. Low-temperature thermal regeneration process could regenerate saturated PAC from biochemically treated coking wastewater at 250 °C in 30 min, and the regeneration efficiency still reached 80.23% after 16 regeneration cycles [17].

Ultrasonic regeneration is a green physicochemical treatment technology [18]. Sonication causes a series of compression and rarefaction cycles leading to the generation of cavitation bubbles. Millions of these bubbles implode, yielding localized temperatures as high as 5000 °C, pressures of 100 MPa, and free radicals such as •OH, HO_2• and O• [19]. Compared with the carbon loss rate of the high-temperature thermal regeneration method (5–10%), the carbon loss rate of ultrasonic regeneration (<2%) is much lower. Ultrasonic cavitation can produce instantaneous high-temperature, high-pressure, strong shock waves, high-speed microjets, and other extreme physical effects on the local surface of the PAC. Studies on the regeneration of the PAC saturated with 4-chlorophenol (4-CP) [13], aniline [14] or chloramphenicol (CAP) [15] by ultrasound have been previously reported. However, when the ultrasonic regeneration method is used alone for the regeneration of 4-CP or CAP, which are difficult to desorb and degrade, the regeneration effect is not ideal.

By combining low-temperature thermal regeneration technology with ultrasonic regeneration technology, it is expected that the PAC regeneration efficiency can be improved and the carbon mass loss rate can be reduced. In this study, volatile acetone and semivolatile aniline were selected as representative pollutants to investigate the regeneration characteristics of the ultrasonic regeneration method, the low-temperature thermal regeneration method, and a combined approach that uses ultrasonic processing in an organic solvent as a pretreatment for the low-temperature thermal regeneration method. The mechanism of low-temperature thermal regeneration of ultrasonic-enhanced PAC was determined to provide technical support for the utilization and regeneration of the PAC.

2. Materials and Methods

2.1. PAC Characteristics and Preparation of Saturated PAC

The PAC used in the experiment was industrial coal activated carbon (Purchased from Junji Environmental Technology Co., Ltd., Wuhan, China, 200 mesh). It had an iodine value of 705.80 mg/g, a methylene blue adsorption value of 174.71 mg/g, a specific surface area of 624.40 m^2/g, a total pore volume of 0.44 cm^3/g, a mesopore volume of 0.34 cm^3/g, a micropore volume of 0.10 cm^3/g. Before the experiment, the PAC was washed with pure

water and boiled 3 times to remove soluble impurities. The washed PAC was then dried at 105 °C to a constant weight and stored in a dryer for later use.

The representative pollutants selected for the experiment were volatile acetone and semi-volatile aniline, with boiling points of 56.5 °C and 184.4 °C, respectively. To achieve the saturated adsorption equilibrium on the PAC, 1.0 g/L of washed and dried PAC was added to water containing either 500 mg/L of acetone or 100 mg/L of aniline. The mixture was stirred at room temperature (25 ± 2 °C) at 150 rpm for 24 h to ensure that the PAC could reach adsorption equilibrium. The equilibrium adsorption capacity of the PAC for acetone and aniline was 230 mg/g and 58 mg/g, respectively. The saturated PAC obtained after filtration was then put into a freeze dryer for the subsequent regeneration experiment.

2.2. Regeneration Processes

2.2.1. Ultrasonic Regeneration Process

The ultrasonic regeneration of the PAC saturated with acetone and aniline was carried out in an ultrasonic reactor (model KQ-200VDE, Kunshan Shumei Ultrasonic Instrument Co., Ltd., Suzhou, China), which has a maximum output power of 180 W. Pure water (1 L) and 1.0 g of saturated PAC were put into the ultrasonic reaction tank. The water temperature was regulated to the required temperature by the temperature control system of the condenser tube and the ultrasonic reactor. The samples were stirred evenly by a motorized stirrer to avoid PAC precipitation during regeneration. The ultrasonic frequency (20, 40, or 60 kHz), the power (0–180 W), and regeneration time (0 min–180 min) were adjusted as needed for each specific experiment.

The experiments with ultrasonic regeneration in organic solvent were carried out in the abovementioned ultrasonic reactor. The ultrasonic frequency was 40 kHz, the power was 180 W, and the regeneration time was 60 min for aniline and 30 min for acetone. A 1.0 g sample of saturated PAC was added to 1 L of methanol or ethanol to investigate the influence of types and concentrations of the organic solvents on the ultrasonic regeneration effect.

2.2.2. Low-Temperature Thermal Regeneration

The low-temperature thermal regeneration experiments on PAC saturated with acetone or aniline were carried out in a tubular furnace (model OTF-1200X, Hefei Kejing, Hehei, China) under a nitrogen atmosphere. A 1.0 g sample of saturated PAC was placed in a quartz tube. The influence of regeneration temperature (100 °C–200 °C) and regeneration time (5 min–40 min) on the PAC regeneration efficiency and the carbon mass loss rate were investigated under a nitrogen flow rate of 0.8 mL/min–1.0 mL/min and a heating rate of 20 °C/min.

2.2.3. Ultrasonic Pretreatment in Organic Solvent with Low-Temperature Thermal Regeneration

In the combined regeneration process, ultrasonic treatment in organic solvent was used as a pretreatment for a subsequent low-temperature thermal regeneration. Ethanol and methanol were the organic solvents used for the regeneration of the PAC saturated with aniline and acetone, respectively. The parameters for the ultrasonic pretreatment in organic solvent were a power of 180 W, a frequency of 40 kHz, an organic solvent concentration in water of 50%, and a regeneration time of 60 min. The low-temperature thermal regeneration used a nitrogen flow rate of 0.8–1.0 mL/min, and a heating rate of 20 °C/min. The thermal regeneration temperature and time for the PAC saturated with aniline or acetone were 200 °C for 15 min or 150 °C for 30 min, respectively.

2.2.4. Degradation of Aniline by Ultrasound in Pure Water

50 mg/L aniline solution sample was prepared and put into an ultrasonic reaction tank. Under the conditions of 180 W and 40 kHz, the sample was degraded for 3 h, and the concentration of aniline at different interval was measured to calculate the degradation

rate of aniline. In addition, two 50 mg /L aniline solution samples were prepared, and n-butanol and acetic acid were added to the water samples, respectively. The concentration of aniline under different degradation time was determined.

2.3. Analysis Methods

The concentration of aniline was analyzed by a colorimetric method using N-(1-naphthyl) ethylenediamine as the chromogenic agent. The absorbance was measured at 545 nm on a UV-VIS spectrometer (UV-2600; SOPTOP, Yuyao, China). Acetone concentration was determined by UV-Vis spectrophotometer at 268 nm. The specific surface area and pore volume of the PAC were analyzed using a nitrogen gas adsorption–desorption isotherm method with constant temperature gas adsorption at 77 K (Tristar II 3020M; MICROMERITICS, Norcross, USA), the sample was outgassed at 200 °C for 8 h before the N_2 adsorption–desorption experiment. The surface morphology of the PAC was analyzed with a scanning electron microscope (SEM, JEM-2100F, JEOL, Tokyo, Japan). Before SEM analysis, the PAC powder was uniformly pasted to a conductive adhesive and then sprayed with gold to improve the conductivity of the sample.

Equation (1) was used to calculate the equilibrium adsorption capacity q_e (mg/g) of the PAC, where C_0 and C_e are the initial and equilibrium concentration of pollutants (mg/L), respectively, v is the volume of the adsorption/desorption solution (L), w is the dosage of adsorbent used (g).

$$q_e = \frac{(c_0 - c_e)V}{w} \tag{1}$$

The regeneration efficiency (RE,%) and the mass loss rate (η,%) were calculated with Equations (2) and (3).

$$RE(\%) = \frac{q_d}{q_e} \times 100 \tag{2}$$

$$\eta(\%) = \frac{W_t}{W_0} \times 100 \tag{3}$$

where q_d is the adsorption capacity of regenerated PAC (mg/g), and W_0 and W_t are the masses of the PAC before and after regeneration, respectively.

3. Results and Discussion

3.1. Effect of Ultrasonic Regeneration

With the increase in ultrasonic power, the regeneration efficiency of the PAC also increased. When the ultrasonic power was increased from 60 to 180 W, the regeneration efficiency of the PAC adsorbed aniline increased from 45.60% to 62.29%, and that of acetone increased from 30.89% to 45.30%, respectively (Figure 1a). At the same power, the regeneration effect of the PAC which had adsorbed aniline was better, which was ascribed to the relatively lower adsorption equilibrium of aniline compared to acetone (58 mg/g vs. 230 mg/g). In the regeneration process, with the increase in ultrasonic power, the cavitation effect caused by ultrasonic energy was also strengthened continuously. The strong shock waves and high-speed microjets caused by ultrasonic cavitation repeatedly impacted the surface and pores of the PAC [20], which made more aniline and acetone molecules desorb from the PAC.

It can be seen from Figure 1b that the regeneration efficiency of the PAC that had adsorbed aniline was higher at the same frequency compared to PAC that had adsorbed acetone. When the frequency was increased from 20 to 40 kHz, the regeneration efficiency of the PAC that had adsorbed aniline increased from 42.04% to 62.29%, and that of the PAC had adsorbed acetone increased from 30.89% to 45.30%. Increases of the frequency beyond 40 kHz had little effect on the regeneration efficiency. When the ultrasonic frequency was 40 kHz, the regeneration efficiency of the PAC was optimal. Theoretically, with the increase in frequency, the complete cavitation period of the ultrasonic agitation is shortened and the diameter and collapse time of the cavitation bubbles are reduced [18]. As a result, the microjets and microbeams generated by ultrasonic vibrations at lower frequencies should

act on small pores of activated carbon more effectively, and the regeneration efficiency should be improved. After increasing the frequency beyond 40 kHz, the regeneration rate remained basically the same. Due to the restriction of the experimental conditions, the increase in frequency could be continued, but it can be inferred that the increase in frequency may further improve the regeneration rate of the PAC.
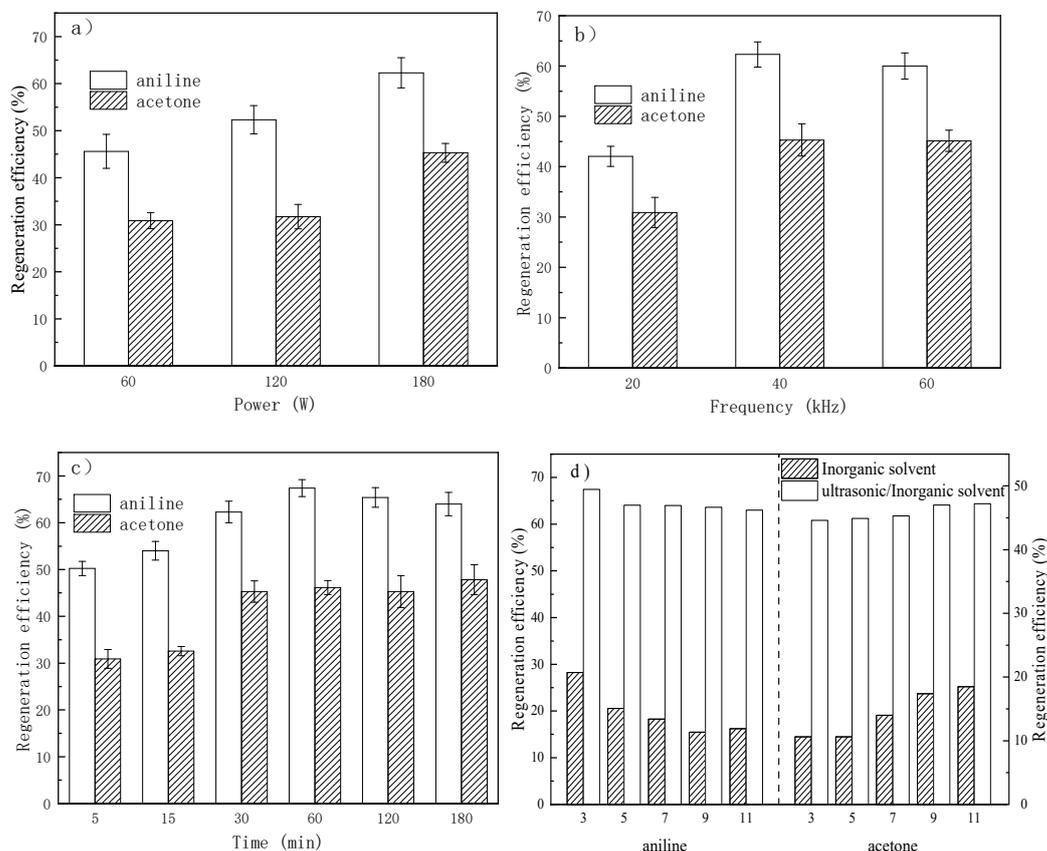

Figure 1. Factors affecting ultrasonic regeneration efficiency. (**a**) Power (frequency of 40 kHz, time of 180 min). (**b**) Frequency (power of 180 W, time of 180 min). (**c**) Time (frequency of 40 kHz, power of 180 W). (**d**) Effect of pH (3, 5, 7, 9, 11) on the regeneration efficiency (power of 180 W, frequency of 40 kHz, time of 180 min).

When the ultrasonic treatment time was increased from 5 min to 60 min, the regeneration efficiency of the PAC which had adsorbed aniline or acetone increased from 50.23% to 67.4% or from 30.89% to 47.84%, respectively (Figure 1c). When the ultrasonic treatment time was longer than 60 min, the regeneration efficiency of the PAC remained basically the same with the prolong of the treatment time. When the ultrasonic treatment time exceeded 30 min, the regeneration efficiency of the PAC that had adsorbed acetone basically did not change as the time was increased. After a certain duration of ultrasonic treatment, the concentration of cavitation bubbles in the solution was saturated. At this point, the high-temperature and high-pressure microjets and shock waves caused by cavitation bubble collapse could not further promote the desorption of the aniline or acetone. Additionally, the long ultrasonic treatment may also cause changes in the specific surface area of the PAC, thereby causing a decline in the adsorption ability of the PAC [13]. The results showed that the regeneration efficiency of the PAC could be improved by prolonging the ultrasonic treatment time properly, but after a certain regeneration time was reached, the regeneration efficiency of the PAC remained basically unchanged, and even decreased in some instances.

The effect of pH on the ultrasonic regeneration is shown in Figure 1d. Under the condition of mechanical stirring without ultrasound, the regeneration efficiency of the PAC

adsorbed with aniline decreased slightly with the increase in pH, while the regeneration efficiency of the PAC adsorbed with acetone increased slightly with the increase in pH. After ultrasound regeneration with varied pH, the regeneration efficiency of the PAC remained basically unchanged.

3.2. Effect of Ultrasonic Treatment in Organic Solvent on Regeneration

It can be seen from Figure 2 that during ultrasonic regeneration in methanol, the regeneration effect of the PAC that had adsorbed aniline was basically not influenced by the methanol concentration. When the methanol concentration was increased from 0% to 100%, the regeneration efficiency only increased from 67.4% to 72%. However, the regeneration efficiency of the PAC that had adsorbed acetone gradually increased with the increase in the methanol concentration. When the methanol concentration was increased from 0% to 50%, the regeneration efficiency increased significantly from 45.30% to 62.32%. When the methanol concentration was further increased, the regeneration efficiency of the PAC that had adsorbed acetone remained basically unchanged.
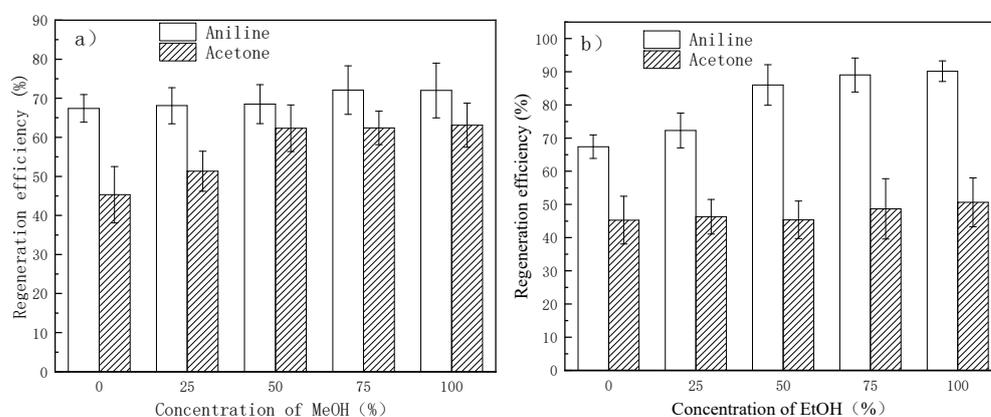

Figure 2. Effect of organic solvent and concentration on ultrasonic regeneration efficiency. Ultrasound power of 180 W, frequency of 40 kHz, time of 180 min. (**a**) Influence of methanol concentration. (**b**) Influence of ethanol concentration.

When the ultrasonic treatment in ethanol was used for regeneration, the regeneration efficiency of the PAC that had adsorbed acetone remained basically unchanged, indicating that ethanol could not promote the desorption from the PAC. When the ethanol concentration was increased from 0% to 100%, the regeneration efficiency only increased from 45.30% to 50.62%. The ethanol concentration had a great influence on the regeneration efficiency of aniline-adsorbed PAC. When the ethanol concentration was increased from 0% to 50%, the regeneration efficiency of the PAC that had adsorbed aniline increased from 67.4% to 86.03%, and the regeneration efficiency changed little when the ethanol concentration was increased beyond 50%.

The instantaneous high-temperature and high-pressure microjets and shock waves caused by ultrasonic cavitation enhanced the contact between organic solvents and pollutants adsorbed on the PAC, which effectively promoted the desorption of pollutants from the PAC [15]. Due to the different polarities of the organic solvents, the desorption effects were different when different pollutants were adsorbed. Therefore, it is necessary to select the appropriate organic solvents for the specific pollutants to be removed.

3.3. Effect of Low-Temperature Heating Regeneration

As shown by the comparison of regeneration effects at different temperatures for 30 min of the low-temperature thermal regeneration in Figure 3. When the regeneration temperature was 150 °C, the regeneration efficiency of the PAC that had adsorbed aniline was only 61.15%. When the regeneration temperature was increased from 150 °C to 200 °C, the regeneration effect improved significantly, from 61.15% to 101.56%, and the adsorption

capacity of the PAC was completely restored. When the temperature was increased from 120 to 150 °C, the regeneration efficiency of the PAC that had adsorbed acetone increased greatly from 45.3% to 89.37%. When the temperature was further increased to 200 °C, the adsorption capacity of the PAC was basically recovered to the level of the original PAC. With the increase in the thermal regeneration temperature, the mass loss rate of the PAC that had adsorbed aniline or acetone increased continuously. When the temperature was increased from 100 °C to 200 °C, the mass loss rate of the PAC that had adsorbed aniline increased from 1.1% to 2.8%, an increase of 154.5%. When the temperature was increased from 120 °C to 200 °C, the mass loss rate of the PAC that had adsorbed acetone increased from 2.4% to 3.6%, an increase of 50%.
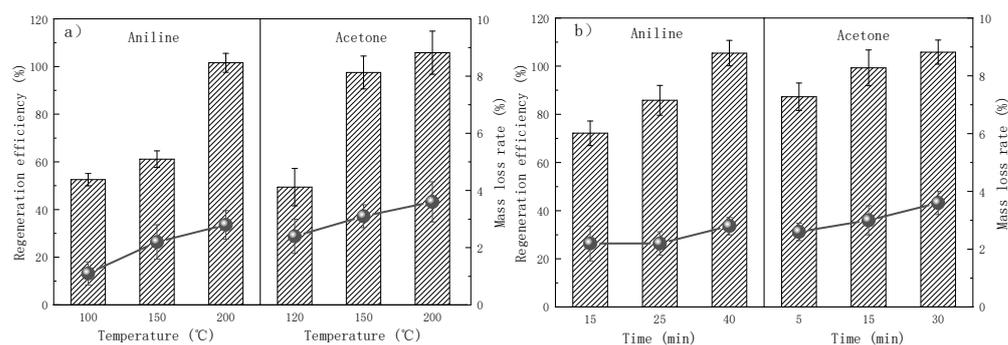

Figure 3. Effect of temperature and process time on low-temperature thermal regeneration efficiency. (**a**) Influence of temperature, time of 30 min. (**b**) Influence of time, temperature of 200 °C.

The regeneration efficiency of the PAC that had adsorbed aniline or acetone increased continuously as the time of the low-temperature thermal regeneration at 200 °C was increased, as shown in Figure 2b. When the regeneration time was increased from 15 min to 40 min, the regeneration efficiency of the PAC that had adsorbed aniline increased from 72.16% to 105.42%, an increase of 42.09%. When the regeneration time was increased from 5 min to 30 min, the regeneration efficiency of the PAC that had adsorbed acetone increased from 80.04% to 96.99%, an increase of 21.18%. With the increase in the thermal regeneration time, the mass loss rate of the PAC increased gradually. When the regeneration time was increased from 15 min to 40 min, the mass loss rate of the PAC that had adsorbed aniline increased by 27.27%, whereas when the regeneration time was increased from 5 min to 30 min, the mass loss rate of the PAC that had adsorbed acetone increased by 38.46%.

3.4. Effect of a Combination of an Ultrasonic Pretreatment in Organic Solvent Followed by Low-Temperature Regeneration

The effect of combined regeneration method, consisting of a combination of an ultrasonic pretreatment in an aqueous organic solvent solution followed by low-temperature heating, was noticeably better than that could be achieved with thermal regeneration alone, as shown in Figure 4. Compared with thermal regeneration for 15 min, the regeneration efficiency of the PAC that had adsorbed aniline increased from 72.20% to 102.40%, an increase of 41.83%, indicating that the ultrasonic pretreatment in ethanol (50% aq.) effectively improved the regeneration efficiency of the PAC. Similarly, the effect of the combined regeneration method on PAC that had adsorbed acetone was much better than that of thermal regeneration alone. It is worth noting that the adsorption capacity of the PAC that had adsorbed aniline could be completely regenerated after 40 min of thermal regeneration, while only 15 min was required to achieve the same effect by the combined regeneration method, which shortened the thermal regeneration time by 62.5%, showing that ultrasonic pretreatment in aqueous ethanol could effectively shorten the subsequent time required for low-temperature thermal regeneration. Similarly, when ultrasonic pretreatment in methanol (50% aq.) was used for the PAC that had adsorbed acetone, the effect of the subsequent thermal regeneration at 150 °C for 30 min was better than that of using ther-

mal regeneration alone (200 °C for 30 min), indicating that ultrasonic pretreatment in an aqueous solvent solution effectively reduced the temperature required for the subsequent low-temperature thermal regeneration. Ultrasonic cavitation was more likely to occur under the synergistic effects of ultrasonic vibration and organic solvents [20]. The high-speed microjets and high-pressure shock waves caused by cavitation impacted the PAC surface and pores more frequently, which promoted the desorption of aniline on PAC, effectively shortened the subsequent thermal regeneration time, and reduced the energy consumption of thermal regeneration.
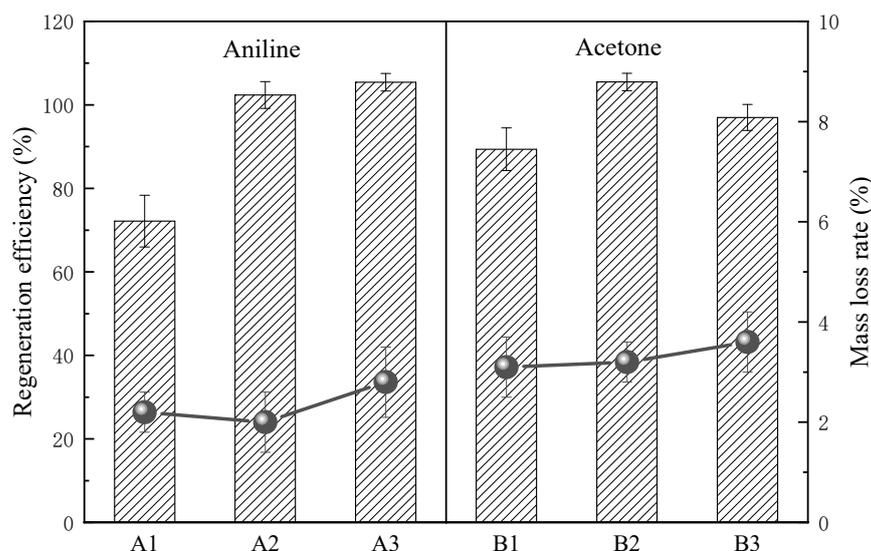

Figure 4. Regeneration efficiency of the combined method of an ultrasonic pretreatment with 50% aqueous solutions an organic solvent (ethanol (EtOH) or methanol (MeOH)) followed by low-temperature heating (A1: thermal regeneration, 200 °C, 15 min, A2: ultrasonic/ethanol–thermal regeneration, 200 °C, 15 min, A3: thermal regeneration, 200 °C, 40 min, B1: thermal regeneration, 150 °C, 30 min, B2: ultrasonic/methanol-thermal regeneration, 150 °C, 30 min, B3: thermal regeneration, 200 °C, 30 min).

The mass loss rate of the PAC regenerated by the combined regeneration method also decreased significantly. Compared with the mass loss rate by thermal regeneration for 15 min, the mass loss rate of the PAC that had adsorbed aniline and then was treated by the combined regeneration method with low-temperature heating for 15 min decreased slightly from 2.2% to 2.0%. Compared with the mass loss rate from thermal regeneration for 40 min, the mass loss rate of aniline-saturated PAC by the combined regeneration method using aqueous ethanol with low-temperature heating for 15 min decreased significantly, from 2.8% to 2.0%, a decrease of 28.6%. Due to the decrease in the subsequent low-temperature thermal regeneration temperature, the carbon mass loss rate of the PAC pretreated by the ultrasonic process with aqueous methanol was obviously less than that of low-temperature thermal regeneration alone (200 °C for 30 min). The ultrasonic pretreatment with aqueous solvent efficiently desorbed aniline and acetone from the PAC, and the presence of organic solvent reduced the threshold value needed for ultrasonic cavitation.

3.5. Regeneration Mechanism (Using Aniline as an Example)

The pore structure parameters of the PAC are shown in Table 1. The N_2 adsorption–desorption isotherms of the PAC before and after regeneration are shown in Figure 5. After adsorbing aniline, the specific surface area and the micropore volume of the PAC decreased. However, for saturated PAC after ultrasonic regeneration, the mesopore volume increased from 0.34 cm^3/g to 0.37 cm^3/g, which indicated that the ultrasonic wave could change the pore structure of the PAC, resulting in an increase in mesopore volume. Compared with PAC regenerated by ultrasonic treatment alone, the specific surface area of the PAC

regenerated by ultrasonic treatment with aqueous ethanol also increased significantly, from 505.83 m^2/g to 582.04 m^2/g. Compared with ultrasonic regeneration alone, the ethanol-enhanced ultrasonic regeneration could restore the specific surface area of the PAC more efficiently. Compared with unused PAC, the mesopore volume of the PAC regenerated by ultrasonic treatment increased from 0.34 cm^3/g to 0.37 cm^3/g, which indicated that the ultrasonic action caused an expansion of the mesopores of the PAC. The expansion of the mesopores regenerated by the ethanol-enhanced ultrasonic regeneration was more obvious. Compared with unused PAC, the total pore volume and mesopore volume of the PAC regenerated by ultrasonic treatment in aqueous ethanol increased by 4.35%, 20.93%, respectively. The microjets and shock waves caused by the collapse of cavitation bubbles during ultrasonic treatment played a major role in the PAC regeneration process. The high-speed microjets and high-pressure shock waves produced by cavitation bubble collapse mainly acted on the PAC surface and mesopores. Under the joint action of the ultrasonic treatment and the ethanol, the microjets and shock waves acted more intensely on the surface and mesopores of the PAC than when ethanol was not used.

Table 1. Pore structure parameters of the PAC.

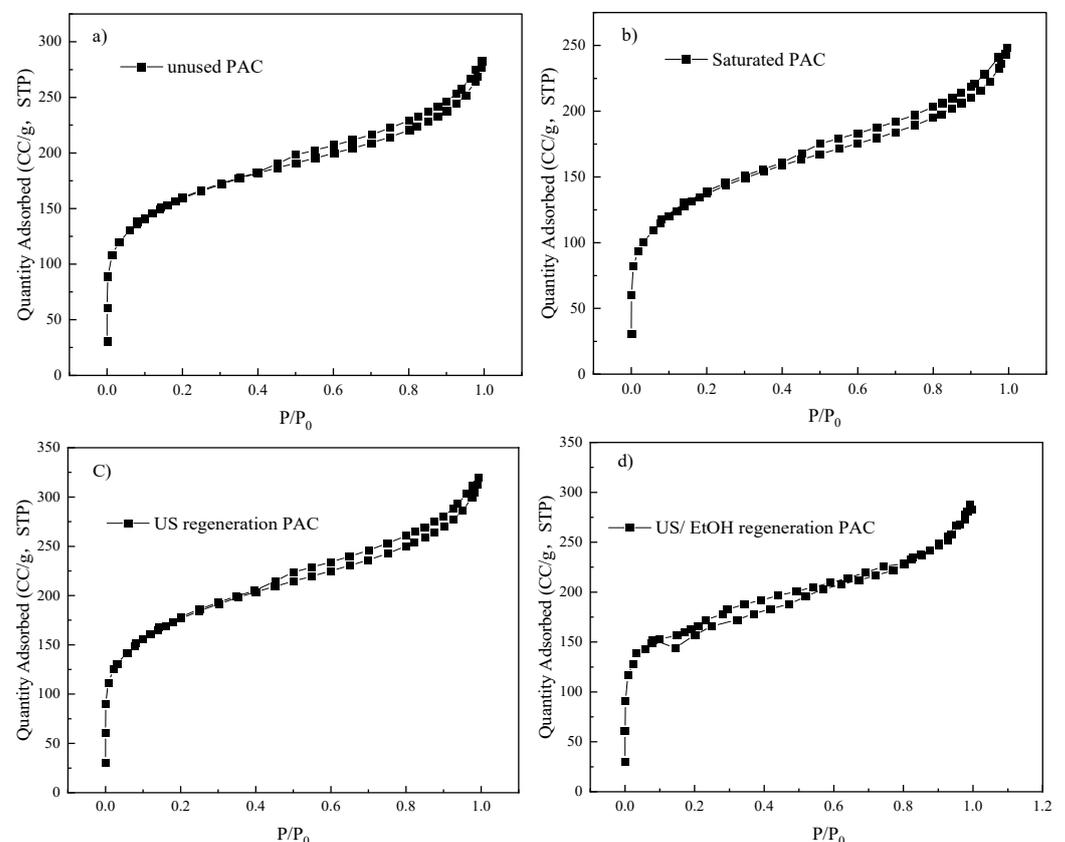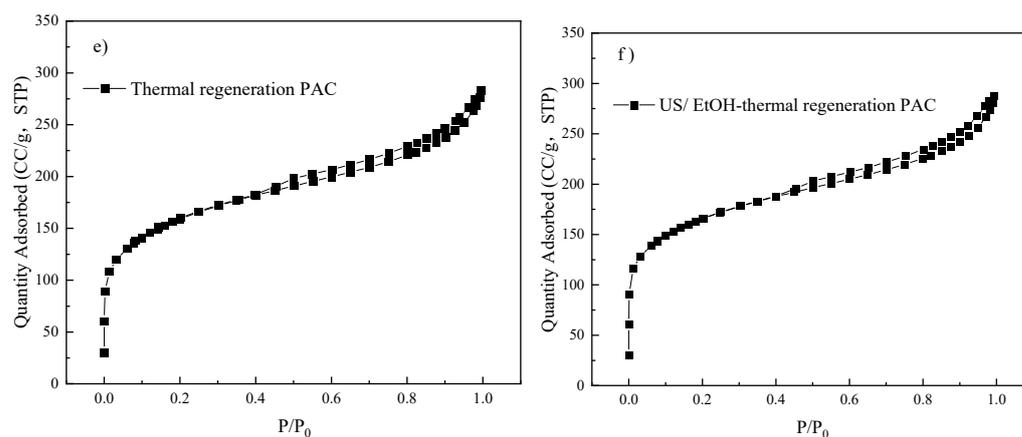| PAC Type	BET Specific Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Micropore Volume (cm^3/g)	Mesopore Volume (cm^3/g)
Unused	624	0.44	0.10	0.34
Saturated	506	0.38	0.04	0.34
US regeneration	537	0.41	0.04	0.37
US/EtOH regeneration	582	0.46	0.03	0.43
Thermal regeneration	627	0.49	0.09	0.41
US/EtOH-thermal regeneration	602	0.44	0.12	0.32

Figure 5. *Cont.*

Figure 5. N2 adsorption–desorption isotherms of the PAC before and after regeneration. (**a**) Unused PAC. (**b**) PAC saturated with adsorbed aniline. (**c**) PAC regenerated by ultrasonic treatment. (**d**) PAC regenerated by ultrasonic treatment in ethanol. (**e**) Thermally regenerated PAC. (**f**) PAC treated by the combined regeneration process.

The specific surface area of thermally regenerated PAC (627 m^2/g) was basically the same as that of the unused PAC (624 m^2/g). In addition, the total pore volume increased by 11.4 %. The above results indicated that thermal regeneration could effectively restore the pore structure of the PAC. The specific surface area and total pore volume of thermally regenerated PAC all increased. The specific surface area of the PAC regenerated by the combined regeneration treatment of ultrasonic pretreatment in an aqueous ethanol solvent followed by low-temperature heating was restored to its initial levels. Both the unused and regenerated PAC had the same total pore volume, while the micropore volume of the regenerated PAC increased from 0.10 cm^3/g to 0.12 cm^3/g. Micropores are the main area where adsorption occurs [21], so the adsorption capacity of the PAC could be restored efficiently by the combined regeneration treatment. Under the synergistic effect of ultrasonic vibration in the presence of the solvent, the microjets and shocks wave acted on the PAC surface and mesopores more frequently, resulting in an increase in mesopore volume and pore size [22], which created good conditions for subsequent thermal regeneration. Therefore, the combined regeneration method effectively improved the PAC regeneration efficiency, reduced the energy consumption, and lowered the mass loss rate of the PAC.

SEM micrographs of the PAC regenerated by different methods are shown in Figure 6. The surface of the unused PAC was smooth, but there were many impurities on its surface after the adsorption experiments, which was likely due to ultrafine particles resulting from the PAC erosion during the stirring of the suspension. After ultrasonic regeneration, the number of fine particles increased due to the further destruction of the activated carbon by the high-speed microjets and high-pressure shock waves caused by the ultrasonic treatment.

The contribution of ultrasonic cavitation to the degradation of aniline in water was studied at an ultrasonic power of 180 W, a frequency of 40 kHz, an ultrasonic treatment time of 180 min, and an aniline concentration of 50 mg/L. It can be seen from Figure 7 that the degradation efficiency of aniline increased continuously with the increase in the ultrasonic treatment time. The degradation rate of aniline reached 17.2% when the ultrasonic treatment lasted for 180 min, which indicated that aniline was partially degraded by the ultrasonic treatment. In a subsequent test, n-butanol and acetic acid were added into water samples as •OH inhibitors, where n-butanol could effectively remove free radicals in the interface area between the gas phase and cavitation bubbles and acetic acid mainly reacted with •OH in the solution [23,24]. It can be seen that the addition of n-butanol or acetic acid reduced the degradation efficiency of aniline from 17.2% to 6.6% or 16.0%, respectively. The inhibitory effect of n-butanol was stronger than that of acetic

acid, indicating that the degradation reaction mostly occurred at the interface area between cavitation bubbles.
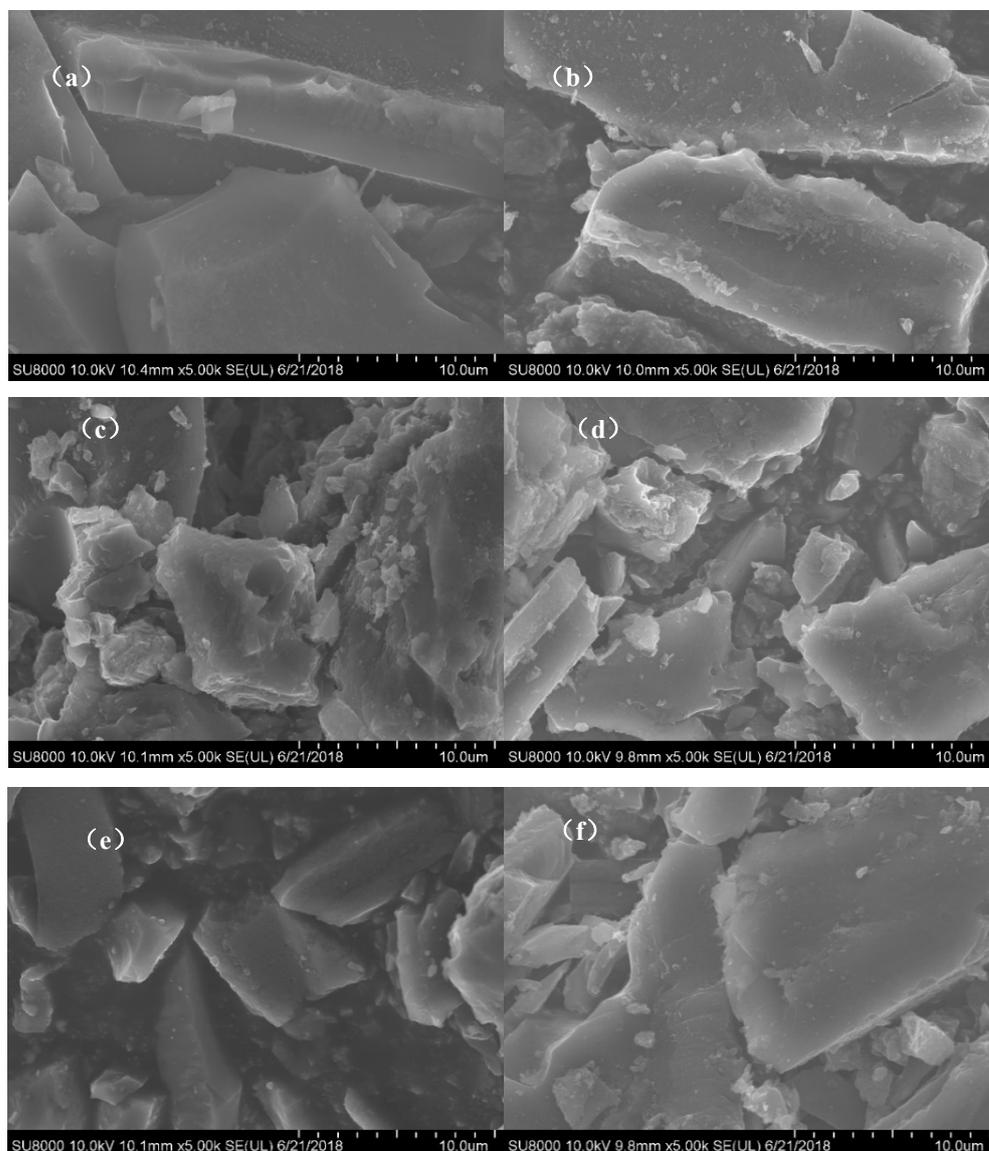

Figure 6. SEM of the PAC before and after different treatments. (**a**) Unused PAC. (**b**) PAC saturated with adsorbed aniline. (**c**) PAC regenerated by ultrasonic treatment. (**d**) PAC regenerated by ultrasonic treatment in ethanol. (**e**) Thermally regenerated PAC. (**f**) PAC treated by the combined regeneration process.

The aniline degradation by ultrasonic in the pure water medium was measured with gas chromatography-mass spectrometry [25], and the primary degradation product detected was azobenzene. Aniline has two degradation mechanisms: the formation of symmetrical azo bonds, and the formation of nitrobenzene [26]. Only azobenzene, a related product, was detected in the degradation product, which may be formed due to the formation of iminobenzene free radicals after aniline loses an electron when attacked by •OH. This kind of imino group is sensitive to substitution reactions, and azobenzene can be formed by the imino group through oxidation and two-electron coupling [27]. In the experiment, products such as nitrobenzene, phenol, and benzoquinone were not detected, indicating that azobenzene was not further degraded, and the ultrasonic cavitation effect could not completely decompose aniline.
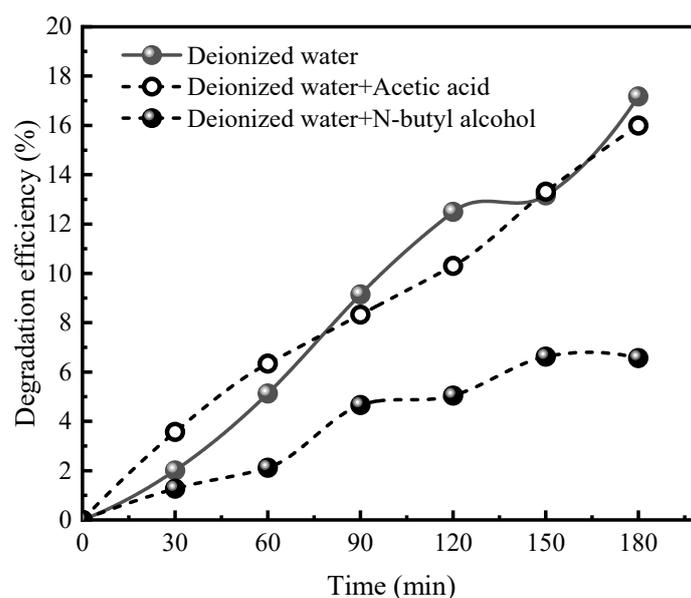
Figure 7. Degradation efficiency of aniline by ultrasonic cavitation.

4. Conclusions

(1) The regeneration effect of the PAC saturated with acetone or aniline can be improved with an increase in ultrasonic power, and the regeneration effect of aniline is better than that of acetone at the same power. There exists an optimum frequency (40 kHz), at which the regeneration effect of both aniline and acetone is the best (62.3% for aniline, 45.3% for acetone). When the regeneration time reaches a certain value (60 min for aniline, 30 min for acetone), the regeneration efficiency of the PAC is basically unchanged, and even decreases. The concentration and properties of organic solvents significantly affect the ultrasonic regeneration of the PAC saturated with aniline or acetone. The regeneration efficiency of both acetone- and aniline-adsorbed PAC increases with the increase in the ethanol concentration, reaching a maximum regeneration efficiency of 86.0%.

(2) With the increase in the heating temperature and the regeneration time, the regeneration efficiency of the PAC saturated with aniline or acetone increases, and the mass loss of the PAC increases noticeably. At 200 °C, when aniline- and acetone-adsorbed PAC are thermally regenerated for 40 min and 30 min, respectively, the adsorption ability of the PAC in both cases can be restored to its original level.

(3) Under a condition of 100% regeneration efficiency, the ultrasonic pretreatment in aqueous ethanol can decrease the thermal regeneration time of aniline-adsorbed PAC from 40 min to 15 min and reduce the mass loss rate by 28.6%. The ultrasonic pretreatment in aqueous methanol can reduce the thermal generation temperature of acetone-adsorbed PAC from 200 °C to 150 °C. The combined regeneration process of an ultrasonic pretreatment in an aqueous organic solvent solution followed by low-temperature heating can effectively improve the PAC regeneration efficiency, lower the energy consumption, and reduce the PAC mass loss rate.

(4) The ethanol-enhanced ultrasonic regeneration of aniline-adsorbed PAC can effectively restore the specific surface area of the PAC, expand the mesopore volume, and increase the pore size, which makes the surface morphology of the PAC coarser. However, with the combined regeneration treatment, PAC agglomeration can be avoided and there are fewer impurities on the surface of the PAC, which are all related to the microjets and shock waves of the cavitation caused by ultrasonic agitation. The degradation efficiency of aniline in water by ultrasonic cavitation and •OH mostly occurred at the interface area between cavitation bubbles reached 17.2%, and the primary degradation product was azobenzene.

(5) The characteristics and the adsorption processes of organic compounds with low boiling points are quite different. Therefore, it is necessary to select the regeneration solu-

tion reasonably and optimize ultrasonic treatment conditions to create favorable conditions for low-temperature thermal regeneration of the PAC saturated with organic compounds with low boiling points.

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