Study on Adsorbents Prepared from Walnut Shells by Supercritical CO_2 Fluids

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Abstract: Adsorbents prepared by supercritical CO_2 fluids (SCF) extraction technique from walnut shells were discussed. The effects of extraction temperature, extraction pressure, and extraction time on the adsorption properties were investigated and obtained the optimum conditions of extraction temperature45 ℃, extraction pressure 35MPa and extraction time 2h. These adsorbents have higher activity (BET, 930 m^2/g, total pore volumes, $6.11\times10^{-3}m^3/g$). When they were used for rolling oily wastewater treatment, the oil content was reduced to 3.70 mg/L, turbidity to 1.76 NTU, and realized 100% of oily wastewater reuse.

Keywords: adsorbents; supercritical carbon dioxide extraction; walnut shell; oily wastewater treatment

1 Introduction

At present, a large amount of carbonaceous agricultural sub-products or wastes, such as walnut shell, coconut shell, sawdust, and various fruit stones produced are currently being extensively studied because of their cheapness, and intrinsic value. Preparation of activated carbon is proposed to as a prospective method to economically utilize because they have relatively high fixed-carbon content (about 18 wt %), low ash content (less than 1.0 wt %), and the presence of inherent pore[1,2]. Activated carbons are widely used as adsorbents for the removal or reduction of pollutants from the exhaust gases and wastewater of industrial sources.

Adsorbents from walnut shell have been widely used for oily wastewater treatment because of their special properties, such as great hardness, wear resistance, high compressive strength (up to 23.4 kgf/cm^2), chemical stability (resistant to acid or base), capacity to remove pollutants with an adsorption rate of 27-50%, great hydrophilicity, resistance to oil immersion and corrosion, etc. In addition, they have a density greater than water, thereby allowing for easy back washing, even with unfiltered water at a low cost[3~5].

Generally, walnut shell can be converted into activated carbons by pyrolysis, physical or chemical activation, in which chemical agents are added to accelerate activation. Although the process is simple, adsorption performance of this adsorbents are inefficient in wastewater treatment for the removal of oil, poisons and other harmful substances. In addition, problems can arise during their application, such as caking, loss of the filtering materials (or adsorbents) themselves and secondary pollution of the water caused by back washing, and so on[6,7].

Aik Chong Lua and Jia Guo developed the preparation methods including two-step CO_2 activation, one-step CO_2 activation and chemical activation with KOH impregnation. The effects of the heating temperature and hold time on the properties of the chars and activated carbons were investigated. The highest BET surface area was up to 894.70 m^2/g[8]. Juan F. Gonza´lez, et al. prepared walnut adsorbents with high pore volumes and a variety of pore size distributions can be produced from walnut shells by tailored CO_2 or steam activation. The highest BET surface area was over 1000.00 m^2/g[9].

Supercritical separation technology is the adjustment of supercritical fluid pressure and temperature to control solubility and vapour pressure. When reduce the density of extraction and separation, the organic materials achieve the separation from supercritical fluid. And maintain material on supercritical fluid circulation [10-11].

Because of these physic-chemical properties and its supercritical conditions at 7.4MPa and 31℃, supercritical carbon dioxide is well adapted to the fractionation and purification of biomolecules and polymers.

The aims of this study are using supercritical CO_2 fluids (SCF) to extract oil, brown pigment and other organic matters,[12] and at the same time, prepare more pore materials (or adsorbents) from walnut shell. These adsorbents can be used to oily wastewater treatment. Because a high rate of re-activation is easy to achieve using supercritical fluids, online activation can be realized during the oily wastewater treatment process, and problems related to back washing of the filtering materials can be resolved. Meanwhile, recycling and reutilization of walnut shell waste is also achieved, which conforms to ecological and environmental protection standards.

2 Materials and Methods

2.1 Materials

The raw materials are fine quality walnut shells which are screened out during pretreatment. The raw materials were divided into two levels in sizes of 0.45-0.9 mm and 0.9-2.5 mm. Another (same sizes) disposed by chemical method would be used in contrasting experiments. The supercritical fluid is CO_2, with purity greater than 99.5%. CCl_4 (the degree of chemical analysis) was used for oil content analysis. The oily wastewater samples contained oil (54.5 mg/L) and turbidity (84.8 NTU) came from steel industry.

2.2 Equipments

Experimental equipment: HA121-50-05 Supercritical CO_2 Extraction Equipment, including the boost system, extraction system and separation system, was used for extraction. The characteristic parameters of the filtering materials or adsorbents, such as specific surface area, total pore volume, and aperture were measured by the nitrogen adsorption method, using an AUTOSORB-1C aperture distribution and specific surface area determinator produced by the US Canta company. The oil content was measured by the OIL2 analyzer.

2.3 Experimental Set-Up

Compressibility is the most important feature of supercritical carbon dioxide. Even a subtle change in pressure and temperature can result in significant changes in density. The ability of supercritical carbon dioxide to dissolve organic matter depends mainly on its density, that is, solubility increases with an increase in density, and decreases, or is even lost, as the density decreases. Therefore, extraction and separation can be achieved by manipulation of the pressure and temperature.

The pretreated walnut shell particles are placed within the reactor and the temperature and pressure adjusted to the supercritical level. The organic materials (mainly fat and oil) are separated from the walnut shells by adjusting the flow rate of carbon dioxide, the pressure, temperature and extraction time, so that the walnut shells are activated and the resulting walnut shell filter materials are obtained.

The supercritical carbon dioxide containing the dissolved oils and fats is then returned to a standard pressure gas by throttling expansion as it passes through a dropping valve, and the oils are separated from the carbon dioxide. In this way, the total pore volume and specific surface area of the walnut shell filter materials are increased. The oil or brown pigment obtained following extraction can be collected after the separation as a high added value by-product [12], and the carbon dioxide gas is then cooled and recycled.

The process flow diagram for the preparation of the walnut shell filter materials is presented in Fig.1.

These filter materials prepared with SC CO_2 were used oily wastewater treatment. The experiments utilized the flocculation- adsorption filtration duplex process for removal of oil and turbidity from the wastewater. Following flocculation, the raw water was separated by the inclined tube, where turbidity was reduced below 10 NTU. The supernatant then flowed through the filters at a velocity of 47.6 ml/min (a natural flow). The filtration velocity was 25 m/h, and processing time was 10 hours. Thus, the oil content and turbidity of the wastewater were measured and comparative analysis was carried out.

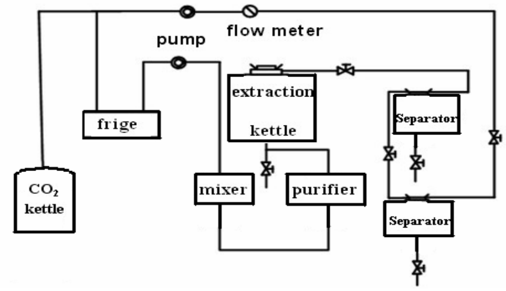

Fig.1 Schematic flow sheet of the preparing process

3 Results and Discussion

Determination of the optimum process parameters for the preparation of walnut shell filtering materials by supercritical carbon dioxide extraction is very important. The main factors influencing supercritical carbon dioxide extraction for the production of walnut shell filtering material are activation temperature, activation pressure and activation time. The single-factor experimental method is used to determine the optimum process parameters based on a comprehensive analysis.

3.1 The Influence of Activation Temperature

At different extraction pressures, the influence of temperature on the solubility varies. When the pressure is high, the density of the supercritical CO_2 is higher and the compressibility is lower. The density of the supercritical CO_2 decreases less as the temperature rises, but it greatly increases the vapor tension and diffusion coefficient of the components to be separated, so that the dissolving capacity is increased. On the other hand, at the critical point where the pressure becomes lower and the compressibility of the supercritical CO_2 is greater, the density decreases sharply when the temperature rises. At this point, although the volatility and diffusion coefficients of the components to be separated increases, it is not enough to compensate for the decline in dissolving capacity due to changes in density. Therefore, under high pressure and certain operating conditions[10-12], there exists an optimum reaction temperature. For extraction at the pressure of 35 MPa for two hours at the following temperatures: 40℃, 45℃, 50℃, 55℃ and 60℃, the relationship between temperature and specific surface area, pore volume, and average pore diameter was determined as shown in Fig.2.

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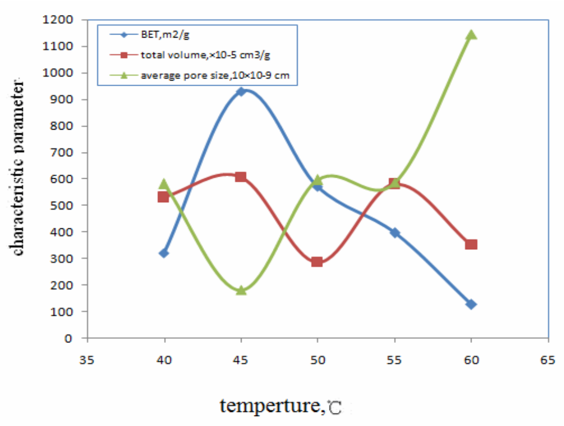

Fig.2 Relationship between activation temperature and specific surface area, pore volume, and average pore diameter.

As shown in Fig.3, at a pressure of 35 MPa, with increasing temperature, the specific surface area initially increased, but then followed a downward trend. At a temperature of 45℃, the specific surface area and pore volume reached their maximum, while the average pore size reached its minimum. This is due to the fact that under the supercritical conditions, a temperature increase will accelerate the movement of CO_2 molecules which improves the efficiency of extraction and increases the number of micropores, so that the specific surface area increases as well. Past a certain critical value (e.g. 45℃), if the temperature continues to increase, the density of the supercritical CO_2 starts to decrease. Within specific pressure limits, the ability of supercritical CO_2 to dissolve oils changes proportionately with its density, such that as the density decreases, so does its capacity to dissolve the extracted oils. As a result, the specific surface area of the walnut shells decreased, and the average pore size first decreased and then increased, while the total pore volume increased, then decreased, then increased again and then finally decreased with the last temperature increase. Through comparative analysis, the result indicate that at a temperature of 45℃, the extraction yield from the walnut shells is the highest, and the activation effect of the walnut shell filtering material is the best.

3.2 The Influence of Pressure

With supercritical carbon dioxide, the solubility of solutes increases with an increase in its density. When the temperature is fixed, the density of carbon dioxide increases with the pressure increases, so as to improve the solubility of the solutes significantly, increase the extraction rate and enhance the activation effect. Unfortunately, better equipment is required and higher operating cost is incurred when running a high pressure system[10]. Therefore it is not desirable to enhance the activation effects by operating at increasing pressure.

With the temperature fixed at 45℃, extraction (activation) of material was carried out for two hours at the following pressures: 25 MPa, 30 MPa, 35 MPa, 40 MPa, and 45 MPa, respectively, and the relationship between pressure and the walnut shell filter's specific surface area, pore volume, and average pore diameter was determined as shown in Fig.3.

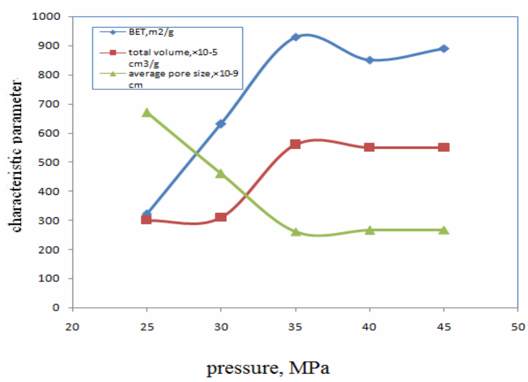

Fig.3 Relationship between pressure and specific surface area, pore volume, and average pore size, respectively.

As seen in Figure 4, at a fixed temperature of 45℃, the specific surface area and total pore volume of the walnut shell filter material increases as the pressure increases, and then levels off after 35MPa. The average pore size decreased as the pressure increased, increasing the extraction yield of oil and other materials from the walnut shells, and enhancing the activity index. However, when the pressure was increased past 35MPa, the volume density increased, and the fluid velocity of the carbon dioxide in the reactor slowed or even reached zero. As a result, mass transfer was affected by the decrease of the diffusion coefficient, leading to a reduction in the efficiency of extraction of the walnut shells' oil and a corresponding reduction in the activation index. Through comparative analysis, a pressure of 35MPa was selected as the optimal parameter.

3.3 The Influence of Activation Time

At a given CO_2 flow volume, the longer the extraction time, the higher the extraction rate, and the better the activation effect. At the start, because the supercritical CO_2 and solutes do not have good contact, there is little extraction. As the process continues, mass transfer improves and the extraction yield in unit time increases until it reaches its maximum. The extraction yield then declines due to a decrease of the components to be separated in the walnut shells, and the activity index changes tend to be slight. It is concluded from the experiment results and the filter material's parameters such as the specific surface area, average pore size, and total pore volume, that as the extraction time proceeds, the performance of the filter material improves significantly. However, the increase in performance tends to level off as the process continues past a certain point. Considering that the oil and fat content of the walnut shells is limited, and in view of cost and effect factors, the determination was made to end the process run after 2 hours.

Therefore, the optimum process parameters under which to prepare activated walnut shell filter material utilizing supercritical CO_2 technology are a temperature of 45℃, a pressure of 35MPa and processing time of 2 hours.

3.4 Properties of Adsorbents

The experiments were based on the measurements of the supercritical fluid extraction filter material's (A) and the chemical extraction filter material's (B) total pore volume, pore-size distribution, and specific surface area[13]. A comparison of the physical properties of the two different filter materials is shown in Table 1.

Table1. A comparison of properties

Filter material	Specific surface area (m^2/g)	Total pore volume ($\times 10^{-3}$ cm^3/g)	Average pore size ($\times 10^{-7}$ cm)
A(supercritical extraction)	930	6.11	2.63
B（chemical extraction)	206	1.76	2.49

As shown in Table 1, the specific surface area of the experimental filter material produced by supercritical CO_2 was determined to be 930 m^2/g, with a total pore volume of 6.11×10^{-3} cm^3/g and an average pore size of 2.62 nm. The specific surface area and total pore volume of the experimental filter material are more than four times that of the chemical extraction filter material, supporting the premise that the walnut shell filter materials prepared by supercritical CO_2 technology have better activation, better oil filtering capacity and pollutant carrying capacity, increase the operational cycle of the filter material and increase treatment capacity.

3.5 Oil Removal of Adsorbents

The filter materials produced by means of supercritical CO_2 were applied in oily wastewater treatment. The oil content and turbidity of the raw wastewater was 54.5 mg/L and 84.8 NTU, respectively. The experiments utilized the flocculation- adsorption filtration duplex process for removal of oil and turbidity from the wastewater. Following flocculation, the raw water was separated by the inclined tube, where turbidity was reduced below 10 NTU. The supernatant then flowed through the filters at a velocity of 47.6 ml/min (a natural flow). The filtration velocity was 25 m/h, and processing time was 10 hours. Thus, the oil content and turbidity of the wastewater were measured and comparative analysis was carried out. The results of the adsorption and filtration are shown in Fig.4.

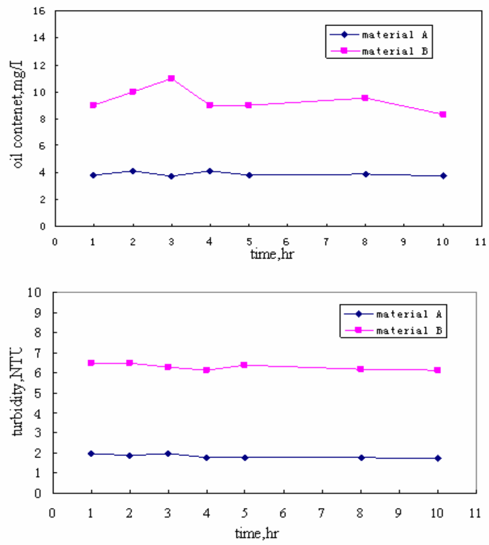

Fig.4 The results of oil removal and turbidity reduction

As can be seen in Fig.4, following treatment, the normal filter material is capable of reducing the wastewater oil content from an original value of 54.5 mg/L, to 8.32 mg/L, and the turbidity from 84.8 NTU to 6.11 NTU. The oil removal rate is 84.73% and the turbidity removal rate is 92.79%. When the experimental filter material is used, the wastewater oil content is reduced from 54.5 mg/L to 3.70 mg/L, equal to a 93.21 % rate removal and the turbidity is reduced from 84.8 NTU to 1.76 NTU or a 97.92% removal rate, which indicates that its capacity for filtering oil and reducing turbidity is greater than that for the normal filter material.

The identical experiments were carried out a second time and following completion the microstructure of the filter material was analyzed by SEM as shown in Fig.8. The left pictures showed the chemical extraction filter material and the right ones the filter material prepared using supercritical fluid extraction technology before treatment (a) and after treatment (b).

Fig.5 showed that after filtration, all the pores of the chemical extraction filter material had been blocked by oil and grease, and no open pore observed. However, the surface of supercritical fluid extraction filter material had a large number of micro-pores, indicating that it still had the capacity to treat additional wastewater. Therefore, it can be concluded that the supercritical fluid extraction filter material has a much greater capacity to bind pollutants than does the chemical extraction filter material.

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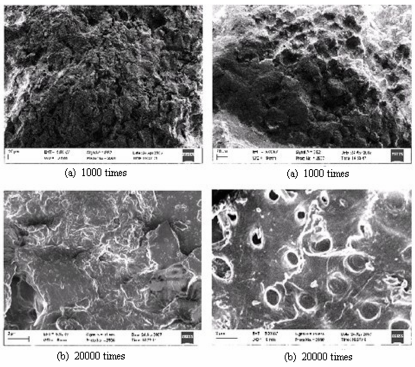

Fig.5 SEM images of the untreated and treated filter materials.

Thus, when the new materials is applied to existing production processes, treatment efficiency will be improved, the frequency of backwashing reduced and the loss of this materials reduced as well, which means a reduction in the cost of wastewater treatment. If the supercritical high-pressure adsorption and filtration tank is used, the operational cycle can be extended as well, and the number of in situ activations can be reduced, so as to avoid problems caused by backwashing.

Adopting the supercritical CO_2 extraction technology for activation [14-15], the parameters were temperature at 45℃, pressure at 35MPa, and processing time of 2 hours. The results indicated that when the oily wastewater had been flocculated and then adsorbed to saturation in the walnut shell filter materials, a better regeneration could be achieved when it was activated in the supercritical CO_2 extraction device. The activity index attenuated very slowly and it was also possible to regenerate repeatedly.

In addition, due to the unlimited solubility of supercritical CO_2 for the oil adsorbed by the filter materials, almost all of the dissolved oil can be separated from the supercritical CO_2 by changing temperature and pressure. The oil can also be recycled.

4. Conclusions

Based on some comparative experiments, the conclusions were drawn as follows.

First, the optimum process parameters for preparation and activation of walnut shell adsorbents by supercritical CO_2 extraction technology were a temperature of 45℃, an extraction pressure of 35 MPa, and an extraction time of 2 hours.

Second, the activity index for adsorbents produced by supercritical CO_2 extraction was 4 times that of the normal materials. The flocculation-adsorption process had obvious advantage in oil removal. In one experiment, the oil content was reduced to 3.70 mg/L, which means recycling of oily wastewater can be achieved.

Third, the technology not only allows for the recovery and recycling of waste resources such as walnut shells, but also oil and other valuable substances can be recycled.

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