Regeneration of Caramel Saturated Activated Carbon jointly by Microwave and Extractive Method

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Abstract

In this study, the spent activated carbon (AC) saturated with caramel was regenerated using solvent assisted with microwave radiation. The efficiency of regeneration was evaluated under parameters such as power and time of microwave radiation, and concentrations and pH of an activator. The quality of regenerated AC (RAC) was assessed by methylene blue (MB) and iodine adsorption. The optimum condition for AC regeneration was under a microwave power of 680 W and 10 min radiation, with 20% ethyl alcohol in the activator and pH of 9–10. Under this condition, the adsorption of iodine and MB on RAC was 878 and 218 mg/g, respectively. The micro structure of RAC was characterized by SEM observation. The surface area of RAC was determined under N2 sorption. The pore size distributions of virgin and RAC determined by Horvath–Kawazoe (HK) and DFT methods resulted in a mean pore diameter of 1.2 nm and a pore volume of 1 cm3/g. A regeneration efficiency of more than 85% could be achieved by microwave assisted solvent regeneration.

KEYWORDS: activated carbon, microwave, regeneration, solvent

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1. Introduction

Activated carbon (AC) has been widely used (Hashemipour et al., 2009; Khataee et al., 2009; Wu et al., 2005; Meshko et al., 2006) as a sorbent due to its great adsorption capacity towards a variety of solutes (Zhang et al., 2008). However, because of its high material cost, regeneration of spent AC becomes necessary to reduce the overall cost. Current available methods for AC regeneration include, but not limited to, chemical and biological (Cal et al., 2000), wet oxidative, ultrasound (Lim and Okada, 2005) and solvent assisted, as well as heat and photo catalytic methods (Ania et al., 2004; Alvarez et al., 2004). Among them, heating regeneration technology was most widely used, but it has many disadvantages such as long regeneration process, high energy input, and low product quality. The use of microwave can mitigate the defects in the process of heating regeneration and reduce the time and energy needed for regeneration. As the heat was generated from the core of the carbon in the microwave processes, the time could be greatly reduced to heat the cold center of the materials. Other advantages of microwave processes include efficient and selective heating, as well as easy automation controls (Menéndez et al, 1999; Van Wyk et al., 1988).

In the microwave field, dipole polarization of polar substances turned electromagnetic energy into thermal energy. If majority of the sorbates saturated on the spent AC were highly polar substances, they would have better capability of absorbing microwave than the sorbent AC. Water and other organic materials adsorbed in the pore space of AC could be easily vaporized and charred after heating, resulting in re-opening of the pore space of AC. In addition, while the AC is heating up under microwave, part of the burning charcoal could be readily released so that aperture expanded and the adsorption activity resumed (Rivera-Utrilla et al., 2003; Leng et al., 1996).

Recently, a microwave-assisted combustion method was successfully used to rapidly synthesize nano-sized α-Al₂O₃ with an average particle size of 96 nm and surface area of 48 m²/g after 15 min heating (Ebadzadeh and Asadian, 2009) and CdO nano-spheres over the time frame of a few min (Selvam et al., 2011). Furthermore, using microwave radiation to replace conventional thermal heating could reduce the overall drying time of cocarboxylase hydrochloride by a factor of 7, which was attributed to the enhanced diffusion of solvents under the influence of microwave radiation (Pinchukova et al., 2011). By employing microwave energy, the regeneration time was considerably shortened compared to
conventional thermal heating (Hejazifar et al., 2011; Franca et al., 2010). For example, methylene blue (MB) adsorption on AC prepared under 10 min microwave activation was higher than that on AC prepared by conventional heating over 60–180 min (Foo and Hameed, 2011). Moreover, microwave heating preserved the porous structure of the regenerated AC (RAC) more efficiently than treatments with a conventional device (Ania et al., 2004). In one study, the regeneration efficiency after the AC was saturated with phenol reached 85.2% in a stirred electrochemical reactor after 5 h of regeneration (Zhang, 2002). Regeneration of AC after coking wastewater treatment using n-pentane could be achieved in 20 min followed by drying the regenerated AC at 150°C for 300 min with the RAC meeting the national emission standard for gas emission treatment and the chemical oxygen demand standard of recycled wastewater in coking plant guidelines after being treated by RAC (Guo et al., 2011).

The stack of spent AC used for discoloring in caramel factories may cause environment pollution and material waste. Thus, regeneration of spent AC becomes a necessity. In this study, the spent AC after saturated with caramel was regenerated using solvent assisted with microwave heating in order to increase the regeneration efficiency and improve the restoration capacity of AC. It was anticipated that this method could improve the product quality after regeneration, reduce the energy cost, and improve regeneration efficiency.

2. Experimental

2.1. Materials

The virgin and spent AC was supplied by Caramel Factory (Xiwang Co., Ltd., Shandong, China). The spent AC was saturated with caramel and contained significant amounts of impurities, such as sand, organic pigments, etc. Reagents used in the study include MB, potassium iodide, sodium phosphate, monopotassium phosphate, anhydrous ethyl alcohol, soluble starch, sodium thiosulphate, potassium hydroxide, and hydrochloric acid. They were purchased from a variety of manufactures and were all of analytical grade.

2.2. Pretreatment of spent AC

In order to separate the impurities such as sand from the spent AC, the pretreatment was carried out to enhance the regenerating effect. Forty g of spent AC was mixed with 100 mL of water containing varying amounts of KOH as the
pretreatment solution. The mixture was agitated at room temperature for 30 min, passed through 150 mesh sieves to remove the sand, and then rinsed with distilled water before being dried.

2.3. Microwave assisted regeneration
A Galanz microwave oven was modified by adding a reflux device to the oven. Four g of spent AC was mixed with ethyl alcohol as activator in a 250 mL volumetric flask. The activator extracted the caramel and other organics from the inner part to the surface of the spent AC, where the microwave could reach. The concentration of ethyl alcohol was 0%, 10%, 20%, 30%, 40%, 50%, 70%, 90%, respectively. The mixture was heated under different microwave powers for a fixed time, different radiation time under a fixed microwave power, or different pH conditions for the activator. After regeneration, the samples were dried under ambient air condition for future tests on efficiencies of AC regeneration. A detailed flow chart of the regeneration process is illustrated in Fig. 1.

![Flow chart of the regeneration process](image)

**Fig. 1.** Technical process for AC regeneration by solvent assisted with microwave radiation.

2.4. Evaluation of regeneration efficiency
The efficiency of AC regeneration was evaluated by adsorption of MB and iodine, a standard method to assess the performance of AC. To a 50 mL flask, 0.100 g AC was mixed with 10.0 mL of 1.5 g/L MB solution. The mixture was oscillated for 20 min, centrifuged, and the absorbance measured at the wavelength of 665 nm. For iodine adsorption, 0.5 g sample was mixed with 10.0 mL of 10% hydrochloric acid and 50.0 mL of 0.1 mol/L iodine solution for 15 min. After filtration, the supernatant was titrated with 0.1 mol/L sodium thiosulfate standard...
solution to calculate the amount of iodine adsorbed. The regeneration efficiency
was determined from the ratio of MB adsorption on RAC over that on virgin AC.

2.5. Methods of material characterization

Surface area (SA) and pore structure of AC were determined using the V-Sorb
2800P surface area and pore size analyzer (Gold APP Instruments Corporation,
China) and Quantachrome Autosorb software. The samples were degassed at 200
°C for 2.5 h. The SA was calculated using the BET method from nitrogen
adsorption at 77 K (Rouquerol et al., 1999) and the pore size distribution was
characterized by the Horvath–Kawazoe (HK) equation (Horvath and Kawazoe,
1983) and the density function theory (DFT) (Macías-García et al., 2006; Khalili
et al., 2000; El-Merraoui et al., 2000).

The surface morphology of the virgin, spent, and regenerated AC was
characterized by a Scanning Electron Microscopy (JSM.5410LV, Japan) to
estimate the efficiency of regeneration as well as the change in pore size and
morphology after regeneration. The Fourier transform infrared spectra of virgin,
spent and regenerated AC were recorded with a Spectrum 100 spectrometer using
KBr pressing method. The spectra were collected by accumulating 256 scans at a
resolution 4 cm⁻¹ in the range of 450 to 4000 cm⁻¹.

3. Results and discussion

3.1. Effect of different experimental conditions on the efficiency of AC
regeneration

One of the factors affecting the efficiency of regeneration was the KOH
concentration in the pretreatment solution. As the KOH concentration increased
from 0 to 50 g/L, the amount of iodine adsorption increased from 760 mg/g to 790
mg/g, and the amount of MB adsorption increased from 176 to 194 mg/g, while
the regeneration efficiency or ratio increased from 73 to 80% (Fig. 2a).

In addition, ethyl alcohol concentration in the activator also had a
significant influence on the effect of AC regeneration. Maximum iodine and MB
adsorption and highest regeneration efficiency was achieved when the alcohol
concentration in the activator was 20 % (Fig. 2b). A further increase in solution
concentration resulted in a systemic decrease in iodine and MB adsorption as well
as the regeneration efficiency.
The effect of radiation time on the efficiency of AC regeneration was evaluated under 0–30 min. Maximum MB and iodine adsorption and the AC regeneration efficiency were obtained at a radiation time of 10 min (Fig. 2c).

Microwave power used for regeneration was another factor that needs to be optimized. The MB and iodine adsorption quickly increases as the microwave radiation power increased from 136 to 680 W (Fig. 2d), suggesting that higher radiation energy can supply the samples with more energy to make a larger activated area and pore space. Excessive power beyond 680 W reduced MB and iodine adsorption as well as the regeneration efficiency. This could be caused by some carbon ablation under at a high energy level of radiation, which might undermine the pore structure.

Fig. 2e showed the pH effect of the activator on the regeneration of AC as indicated by MB and iodine adsorption and regeneration efficiency. When the activator was acidic, both the MB and iodine adsorption was low, with a regeneration efficiency of only 73%. These values increased when the pH of the activator continuously increased to neutral. After the pH of the activator was raised to 9–10, a maximum regeneration efficiency of 88% was achieved in comparison to 50% regeneration efficiency from MB saturated AC after 5 adsorption-desorption cycles by a similar microwave regeneration method under inert atmospheric condition (Foo and Hameed, 2012).
Fig. 2. Effect of KOH concentration in the pretreatment solution (a), the ethyl alcohol concentration in the activator (b), the radiation time (c), microwave radiation power (d), and solution pH (e) on the efficiency of AC regeneration and adsorption of MB and iodine.

3.2. Characterization of activated carbon

SA, pore volume, and pore size distribution are important factors affecting the performance of AC. Larger surface area and pore volume will result in higher adsorption capacity. The nitrogen adsorption on virgin and regenerated AC was significantly higher than that on spent AC, suggesting that virgin and regenerated AC had essentially the same pore structure (Fig. 3). When $P/P_0 \geq 0.08$, the nitrogen adsorption followed a type IV curve. The more prominent adsorption at a relatively high partial pressure suggested more pore space available predominantly by microporous space. The SA calculated from the BET data was
1355, 1058, and 36 m²/g, for regenerated, virgin, and spent AC, respectively. The SA values for virgin and regenerated AC were similar to those of KOH-activated carbons (Khezami et al., 2005). The test results showed a larger SA for RAC in comparison to virgin AC, suggesting an excellent effect of AC regeneration under the assistance of microwave radiation.

![Fig. 3. Adsorption isotherms of N₂ at 77 K.](image)

Pore size distribution obtained using the HK equation and the DFT method (Olivier, 1988) is illustrated in Fig. 4. The pore diameter of virgin and regenerated AC was mainly in the range of 0.8–1.5 nm with a mean diameter at 1.2 nm and a pore volume of 1 cm³/g, based on the DFT method, in comparison to a mean pore diameter of 2.0 nm and pore volume of 0.2 cm³/g for a silica aerogel powder synthesized from oil shale ash in the presence of different surface modification agents under ambient pressure of drying (Gao et al., 2010). The pore diameter of the spent AC was much larger, resulting in a much lower N₂ adsorption capacity. The organic matter, CO, CO₂, water vapor, etc. adsorbed in the pores desorbed after exposure to microwave radiation. The removal of CO, CO₂, water vapor, and other gases would widen the micro-pores slightly (Xiao et al., 2005). As the time for the activation process increased, the micro-pores generated would further widen, forming part of the meso-pores. Due to a fast response to microwave heating, internally generated active sites and other features under microwave radiation could effectively prevent the pores from expanding further (Ania et al., 2004).
The SEM showed that the macro-pore space of the spent, virgin, and regenerated AC was about the same. The pores on the surface were of various sizes and depths. In addition, the surface of AC was uneven. There were some small grains internally and on the surface that were thought to be metal oxide particles or carbon particles from the activation process. These impurities reduced the absorption capacity and the surface area slightly (Fig. 5). The rich pore structure resulted in a large specific SA and strong adsorption capacity.
As the microwave energy was rapidly radiated into the pores of AC, organic matter would be released as part of the combustion gases, and during charring. The pores of spent AC at high temperatures after removal of water and gases would be gradually expanding. On the other hand, with lower microwave energy, the adsorbed organic matter and other volatiles could not be quickly removed from the pores (Zhang and Wang, 2007). Thus, microwave power for the regeneration of AC has a significant impact.

The FTIR spectra of virgin AC, spent AC and RAC are illustrated in Fig. 6. The broader band at 3330 cm\(^{-1}\) could be assigned to the –OH stretching vibration; the strong band at 1575 cm\(^{-1}\) attributed to the C=O stretching of carbonyl group, and the bands at 1179 and 1068 cm\(^{-1}\) were related to the condensed C–C–C bending (Asadullah et al., 2010). These two bands, particularly the 1179 cm\(^{-1}\) band, were stronger for virgin AC and RAC, indicating larger contribution to the total spectra by C–C–C bending of AC. The most significant difference between the spent and virgin or RAC is the appearance of a strong band at 1430 cm\(^{-1}\), corresponding to \(\delta CH_2+\delta COH+\delta CCH\) of \(\alpha\)-D-Glucose or \(\delta OCH+\delta COH+\delta CCH\) of \(\beta\)-D-Fructose monohydrate (Ibrahim et al., 2006). This band was absent for virgin AC and became stronger for spent AC. It was almost absent again after regeneration. The disappearance of this band after regeneration clearly demonstrated the removal of caramel from AC.
3.3. The MB adsorption isotherm on regenerated AC

The MB adsorption isotherm was determined to estimate the parameters of adsorption thermodynamics in order to offer an insight into the surface properties and adsorption mechanisms. The MB adsorption data were fitted to the Langmuir, Freundlich or Temkin isotherms. The Langmuir and Freundlich isotherms were used to characterize the adsorption of MB and phenol on KOH-activated carbons (Khezami et al., 2005). The Langmuir isotherm assumes a homogenous surface with a monolayer adsorption (Langmuir, 1916):

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}
\]  

(1)

where \(C_e\) is equilibrium solute concentration (mg/L), \(q_e\) is the amounts of solute adsorbed (mg/g), \(q_m\) is solute adsorption capacity (mg/g), and \(K_L\) is the Langmuir constant (L/mg).

The Freundlich isotherm is suitable for heterogeneous surfaces and suboptimal absorption. The non-uniformity results from the reaction among different organic functional groups, the sorbents, and the impurities. The Freundlich isotherm can be expressed by the following empirical formula:
\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]  \hspace{2cm} (2)

where \( K_f \text{ (mg/g)} \) is the Freundlich adsorption constant and \( 1/n \) is used to measure the absorption intensity.

The adsorption effect was related to the uniform distribution of adsorption energy by the Temkin equation, which takes the form (Temkin and Pyzhev, 1940):

\[ q_e = \frac{RT}{b} \ln(AC_e) \]  \hspace{2cm} (3)

It can be re-arranged to:

\[ q_e = B \ln A + B \ln C_e \]  \hspace{2cm} (4)

where \( B = \frac{RT}{b} \), \( b \) is a Temkin constant (J·g/mol·mg) related to the heat of adsorption. \( A \) is the Temkin isotherm constant (L/g), \( R \) is the gas constant (8.324 J/mol-K), and \( T \) is the absolute temperature (K).

Fig. 7 shows the fitting of the experimental data to the three isotherms. The fitted parameters are listed in Table 1. Comparison of the goodness of fitting for the three models, Langmuir isotherm was more suitable than the Freundlich and Temkin isotherms. The validity of the Langmuir model confirmed a monolayer surface coverage of the dye on the AC surface and that each dye molecule had the same activation energy (Hameed et al., 2008).

![Fig. 7. Comparison of different isotherms for MB adsorption onto the RAC.](image-url)
Table 1. The parameters of MB adsorption on AC fitted to the Langmuir, Freundlich, and Temkin isotherms.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>q_m (mg/g)</td>
<td>238</td>
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<tr>
<td></td>
<td>K_L (L/mg)</td>
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<tr>
<td></td>
<td>r^2</td>
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</tr>
<tr>
<td>Freundlich</td>
<td>K_f (mg/g)</td>
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<tr>
<td></td>
<td>n</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>r^2</td>
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</tr>
<tr>
<td>Temkin</td>
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</tr>
<tr>
<td></td>
<td>b (J·g/mol·mg)</td>
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</tr>
<tr>
<td></td>
<td>r^2</td>
<td>0.88</td>
</tr>
</tbody>
</table>

4. Conclusions

The results from this study showed that microwave-assisted AC regeneration from caramel-saturated AC could be achieved within 10 min with a regeneration efficiency of 85%. Maximum regeneration efficiency and adsorption of MB and iodine were obtained at a microwave radiation power of 680 W and an activator pH value of 9–10. Under these conditions, the regenerated AC can be used in line with the requirements of national standards (GB/T13803 2-1999).

References


