Study on the preparation of straw activated carbon and its phenol adsorption properties

Liping Chen
College of Chemistry and Environment Science, Inner Mongolia Normal University, Hohhot 010022, China
E-mail: clp@imnu.edu.cn

Abstract. Using sunflower straw as raw materials to manufacture straw activated carbon-modified by phosphoric acid and adsorption isotherm of phenol on straw activated carbon was studied in a batch reactor. The physical properties of the prepared straw activated carbons were characterized by scanning electron microscopy. The effect of various parameters, adsorbent dose, pH and temperature, were studied on optimum conditions. The results have shown that the absorbent was efficient, the removal ratio of phenol up to 99.36% with an adsorbent dosage of 16 g·L⁻¹, a pH of 6.0-8.0, at 25 °C. The experimental adsorption data fitted reasonably well to the Langmuir isotherm, the maximum adsorption capacity was 109.89 mg/g. The process of adsorption is an exothermic process.

1. Introduction
Phenol is a highly toxic organic pollutant, which is harmful to environment and health. Phenol can be absorbed by skin, the digestion tract and the respiratory tract so that short-term exposure of phenol can cause central nervous system, kidney, cardiac muscle, blood and other organ system more acute damage. And phenol also has chronic toxicity for algae, fish and shrimps, which can inhibit the growth of the aquatic life, and even lead to death. Phenol has been registered as priority pollutants in the water quality standards for drinking water by China and Europe and the United States and other countries.

Several methods have been developed to remove phenol from wastewater, main including microbial degradation [1], chemical oxidation [2], photocatalytic degradation [3], membrane separation [4], solvent extraction [5] and adsorption [6]. Yet, still the adsorption technique using activated carbon in dealing with wastewater is the most favorable method due to high adsorption capacity, huge BET surface area, big pore structure and stable chemical properties. At present, activated carbon adsorption method has good removal effect, high adsorption capacity and low operational cost. Commercial activated carbon is not suitable for promotion because of its high cost. So it is necessary to develop activated carbon raw material of low cost and easy acquisition for mass production.

Sunflower straw is a kind of a large amount of waste agricultural production in China, the sunflower has been planted for 1720 km² each year only in Hetao plain, Inner Mongolia, China, and its straw production has reached to one million tons each year. Using sunflower straw as raw material to prepare activated carbon not only wide prospect of straw development but also offers low-cost new activated carbon raw material. The paper is about using the sunflower straw of low cost agricultural production to make the straws activated carbon with the activator of phosphoric acid. Researches have been done for the adsorptive performances to solve phenol pollution problems of wastewater and
provided basic data for research and application of taking sunflower straw as raw material to make activated carbon.

2. Materials and methods

2.1. Preparation and characterization of carbon
The sunflower straw is from Hetao plain, Inner Mongolia, China. The surface dust of sunflower straw was cleaned and then cut into about 2 cm short sections, washed by tap water again, rinsed twice or three times by distilled water at last, baked to dry in the temperature 120 °C in oven, powdered, screened by 20 mesh sieve. The samples were immersed in phosphoric acid solution about 2 h with the ratio 1.5:1 (weight) of phosphoric acid to sunflower straw, baked to dry in the temperature 110 °C in oven, put into tube type furnace, heated under the protection of nitrogen flow to rise temperature with 10 °C/min until to 300 °C, activated for 90 min in this constant temperature, again immersed in 5% HCl for 8 h, washed to about 7 of water’s pH value with distilled water, dried in 110 °C, powdered, screened by 60 mesh sieve, weighed to calculate recovery. In this experiment, dry sunflower straw is 100 g, powder of activated carbon manufactured is 54.2 g, recovery is about 54.2%.

2.2. Measuring adsorbent properties
The morphology of the adsorbents was observed by scanning electron microscopy (Hitachi S-3400 series.). The powder of adsorbents were dispersed and coated on the support film of tape, then used to be determined with test voltage of 20 kV and beam of 5×10⁻⁹ mA.

2.3. Batch Adsorption Studies
Some amounts of adsorbent had accurately been weighted and put into 250 mL conical flask, then 50 mL simulated wastewater containing phenol was added into adsorbent and oscillated for 24 h in the thermostatic water bath oscillators, then taken out, filtered by 0.145 μm microfiltration membrane. The phenol concentration was then measured by UV spectrophotometer (DR-5000, Germany). These three experiments were carried out in duplicates and the average values were reported. The blank experiments’ results showed that the total concentration of phenol changed less than 1%, so the effects of these operating processes can be omitted.

The equilibrium adsorption capacity and adsorption efficiency were calculated as follows:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  
\[ \eta = \frac{C_0 - C_e}{C_0} \times 100\% \]

Where, \( q_e \) is the adsorption capacity of phenol on adsorbent (mg·g⁻¹), \( C_0 \) the initial concentration of phenol solution (mg·L⁻¹), \( C_e \) the equilibrium phenol concentration in solution (mg·L⁻¹), \( m \) the mass of adsorbent used (g) and \( V \) is the volume of phenol solution (L), \( \eta \) the adsorption efficiency (%).

3. Results and discussion

3.1. Scanning electron microscopy
Figure 1 shows Scanning electron microscopy of activated carbon.
From the SEM image can be seen that the morphological characteristics of activated carbon used in the experiment has the uneven surface, porous structure, and pore unobstructed, so as to ensure easy accesses to more phenol activated carbon mesoporous and microporous, also increase the adsorption capacity.

3.2. Effect of adsorbent dosage
The adsorption of the phenol on activated carbon was studied by varying the activated carbon concentration (0.2–1.0 g/50 mL) for phenol concentration of 250 mg/L, adsorption temperature 25 °C, oscillated 120 r/min for 24 h. The percentage of adsorption increased with increase in the activated carbon concentration (Figure 2). This was attributed to increased carbon surface area and the availability of more adsorption sites [7]. When the dosage of activated carbon is 0.4 g, phenol removal rate reached the maximum value of 99.36%.

3.3. Effect of solution pH
The dosage of adsorbent at 16 g·L⁻¹, the concentration of phenol at 500 mg·L⁻¹, adjusted for pH value by 0.1 mol·L⁻¹ HCl and NaOH, the adsorption temperature at 25 °C, and oscillating time at 24 h. The relationship between pH value and the removal rate of phenol or equilibrium adsorption amount may be seen in Figure 3.
Figure 3. Effect of pH on removal of phenol by activated carbon

Figure 3 shows that the adsorption capacity of phenol increased with increase in the pH when pH < 10, and phenol removal rate and adsorption capacity of phenol decrease obviously when pH > 10. When pH is 6-10, phenol removal rate is above 99% and adsorption capacity of phenol is about 30 mg/g, that is to say the removal efficiency is good. The reason may be that phenol exists in molecular state so that the increase adsorption capacity of phenol on activated carbon due to great affinity of straw activated carbon surface. The \( pK_a \) of phenol is 9.96, the decrease in the adsorption capacity of phenol is attributed to both greater solubility of dissociated phenol at pH > \( pK_a \) and increased repulsion forces between the dissociated form of the adsorbate and the carbon surface. Because phenol is weak acidic, the most appropriate pH should be 6-8 in subsequent experiments.

3.4. Adsorptive isotherms

The adsorptive isotherm curves may be seen in Figure 4 when the dosage of adsorbent is at 16 g·L\(^{-1}\), with the initial concentration of phenol from 500 to 900 mg·L\(^{-1}\), pH=6.0-8.0, and oscillating time 24 h.

Figure 4. Equilibrium isotherm data for the adsorption of phenol at different Temperatures for phenol wastewater

Figure 4 shows that the greater the concentration of phenol in the same temperature, the greater the amount of activated carbon adsorption. The higher the temperature, the less the equilibrium adsorption amount, implying an exothermic nature of the adsorption process. And under the conditions of high temperature, dynamic energy of theirs is larger so the adsorbed substances get more easily rid of the control of adsorbent.
3.5. Adsorption model

The distribution of phenol between the solid-solution interface equilibrium has been described by the Langmuir equation was linearized as follows:

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

(3)

Where \( C_e \) is the equilibrium concentration (mg L\(^{-1}\)), \( q_m \) is the monolayer adsorption capacity (mg g\(^{-1}\)) and \( b \) is the constant related to the free adsorption energy (Langmuir constant, L mg\(^{-1}\)). The \( q_m \) and \( b \) values were calculated from the slopes \( (1/q_m) \) and intercepts \( (1/bq_m) \) of linear plots of \( C_e/q_e \) versus \( C_e \) (Table 1).

The Freundlich equation was linearized as follows:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  

(4)

Where \( K_F \) and \( n \) are constants. The \( n \) and \( K_F \) values were calculated from the slopes \( (1/n) \) and intercepts \( \ln K_F \) of linear plots of \( \ln q_e \) versus \( \ln C_e \) (Table 1). It is considered that the \( 1/n \) value between 0.1 and 1 indicates a beneficial adsorption, \( 1/n \) value is more than 2 indicates unfavourable adsorption [8]. Table 1 shows that the Langmuir isotherm model turned out to be extremely satisfactory with the highest \( R^2 \) value (>0.99), compared to the other model. Langmuir equation is based on thus theories: the surface of adsorbent is homogeneous and monolayer adsorption, that is to say a adsorption site corresponds to a adsorbent molecule. Langmuir maximal adsorption capacity is 129.87 mg/g at 45 °C. Statistical analysis suggested that variance analysis significance probability is found to be significant \( (p<0.001) \) and the temperature has significant influence on adsorption of phenol.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, \( R_L \) that is used to predict if an adsorption system is favourable or unfavourable [9]. \( R_L \) is defined by:

\[ R_L = \frac{1}{1 + bC_0} \]  

(5)

Where \( b \) is the Langmuir constant (L mg\(^{-1}\)), \( C_0 \) is the initial concentrations of the phenol(mg L\(^{-1}\)). \( R_L \) values between 0 and 1 indicate favourable adsorption. The values of \( R_L \) at different temperatures are given in Table 1. Table 1 shows that at the temperature between 25-45 °C, initial concentrations of phenol are 500-900 mg/L, \( R_L \) values were found quite close to zero. This situation can also be interpreted as the adsorption of phenol on activated carbon is a relatively irreversible reaction [10].

Table 1. Langmuir and Freundlich isotherms constants

| t (°C) | Freundlich isotherm | Langmuir isotherm |
|-------|---------------------|-------------------|
|       | b      | 1/n | \( R^2 \) | \( q_m \) (mg/g) | \( K_F \) (L/mg) | \( R^2 \) | \( R_L \) |
| 25    | 33.6126 | 0.2432 | 0.9904 | 129.8701 | 0.1959 | 0.9952 | 0.0056−0.0101 |
| 35    | 20.3552 | 0.3398 | 0.9868 | 125.0000 | 0.3398 | 0.9937 | 0.0032−0.0059 |
| 45    | 16.7065 | 0.3755 | 0.9957 | 109.8901 | 0.3755 | 0.9990 | 0.0030−0.0053 |

4. Conclusions

The present study showed that the sunflower straw activated carbon is a promising adsorption for the removal of phenol from aqueous solution. The highest removal rate of phenol on straw activated carbon is 99.37% when the concentration of phenol at 500 mg L\(^{-1}\), adsorbent dosage of 16 g L\(^{-1}\), oscillating time 24 h, pH=6–8, and the adsorption temperature 25 °C. The adsorptive isotherm curves can be fitted with Langmuir equations, and the maximum adsorption capacity of Langmuir is at 109.89 mg/g at 25 °C. The adsorption of phenol is a monolayer chemical adsorption and endothermic process.
Acknowledgements
This work was financially supported by the Hohhot Natural Science Foundation (2014MS0221).

References
[1] El-Naas M H, Al-Zuhair S, Makhlouf S 2010 Batch degradation of phenol in a spouted bed bioreactor system J. Ind. Eng. Chem. 16 267–272.
[2] Yavuz Y, Koparal S 2006 Electrochemical oxidation of phenol in a parallel plate reaction using ruthenium mixed metal oxide electrode J. Hazard. Mater B136 296–302.
[3] Svetlana Ivanova, Anna Penkova, Maria del Carmen Hidalgo 2015 Synthesis and application of layered titanates in the photocatalytic degradation of phenol Applied Catalysis B: Environmental 163 23-29.
[4] Busca G, Berardinelli S, Resini C, Arrighi L 2008 Technologies for the removal of phenol from fluid streams: a short review of recent developments J. Hazard. Mater 160 265–288.
[5] Yang C, Qian Y, Zhang L, Feng J 2006 Solvent extraction process development and on-sitetricl-plant for phenol removal from industrial coal-gasification wastewater Chem. Eng. J. 117 179–185.
[6] Tulaphol S, Bunsan S, Kanchanatip E 2016 Influence of chlorine substitution on adsorption of gaseous chlorinated phenolics on multi-walled carbon nanotubes embedded in SiO2 International Journal of Environmental Science and Technology 13(6) 1465-74.
[7] Namasivayam C, Yamuna R T 1995 Adsorption of direct red by biogas residual slurry Environ. Pollut 89 1.
[8] Namasivayam C, Kanchana N 1992 Waste banana pith as adsorbent for colour removal from wastewaters Chemosphere 25 1691-1706.
[9] McKay G, Blair H S, Garden J R 1982 Adsorption of dyes on chitin. 1. equilibrium studies J. Appl. Polym. Sci. 27 3043-57.
[10] Ghosh D, Bhattacharyya G K 2002 Adsorption of methylene blue on kaolinite Appl. Clay Sci. 20 295–300.