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Adsorption and De-Sorption of Polycyclic Aromatic Hydrocarbons on Activated Carbon

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Abstract

The adsorption and de-sorption properties of polycyclic aromatic hydrocarbons (PAH) which was represented by pure phenanthrene, on activated carbon were investigated. The influences of solvent (acetone, carbon tetrachloride, tetrahydrofuran, ethanol or distilled water), time and manner (with ultrasonic or not) on the desorption efficiency were investigated. The results show that the de-sorption efficiency reaches 91.40% which exhibits the highest efficiency when the ethanol is used as the de-sorption solvent and the system was treated with ultrasonic technology. The desorption test was also carried on the raw coconut shell-based activated carbon and it was not being used before. This determination is to understand the "baseline background" and the purity of raw activated carbon characteristics. The content of total de-sorption amounts was 0.043% of raw activated carbon. Through GC/MS analysis, the main desorption substance defined was 10-undecenoic acid methyl ester.

Keywords: Activated carbon; Adsorption; De-sorption; Phenanthrene; GC / MS

Introduction

Most of the active carbon is black powder or granular amorphous carbon. In addition to its main component carbon, it also contains oxygen, hydrogen and other elements. Activated carbon has large specific surface area and good adsorption characteristics. Activated carbon is often used for water purification including tap water, industrial water, wastewater and pharmaceutical water, gas adsorption, such as air purification, gas purification, and harmful emissions control. In addition, activated carbon is also used in some high demand areas, such as blood purification [1], recovery of precious metals like gold and silver [2] and making high-performance fuel cells [3,4]. Activated carbon almost relates with all industrial sectors of people's daily lives.

With the rapid development of activated carbon industry, the study on adsorption and/or desorption of activated carbon increases rapidly. In literatures, there are many reports about adsorption properties of activated carbon, which include the adsorptions of many compounds and metals, such as methyl tertiary-butyl ether, trichloroethene [5], resorcinol,catechol [6], mercury [7,8], phenanthrene [9], p-nitrophenol [10], naphthalenesulphonic acids [11], aromatics [12], Hg-Ni-Cd metal ions [13] etc. However the report about de-sorption of activated carbon is less [14].

The de-sorption performance of activated carbon is one important aspect of the properties of activated carbon. To research de-sorption of activated carbon is indispensable to fully understand essentials of activated carbon. By application of de-sorption, it can solve the identification of specific substances, which were adsorbed on activated carbon, and provide the necessary information for some specific areas, such as blood purification, food additives and other deep-level activated carbon application.

This study is also relevant with issues of environmental protection. People in modern life give great attention to air purification, especially to purification of industrial emissions. Currently, activated carbon impregnated with catalyst has been used in desulfurization and denitrification [15].

However, the often gas in industrial emissions contain levels of

PAH. Analogously with desulfurization and denitrification processes, key questions to answer are how will the PAH impact to them when carried out by applying carbon-base catalyst? When activated carbon is regenerated, how will the PAH affect the regeneration efficacy? Some PAHs are also carcinogens, and handling of these chemicals requires safety protocols? These environmental issues need to be researched.

According to above needs about deep-level activated carbon application and environmental protection, an exploratory study was made. Firstly, our study focused on adsorption and de-sorption of PAH, especially on the de-sorption characteristics. Through a series of experiments, results obtained show some significance.

Experimental Procedure

Apparatus, reagents and samples

The GC-MS instrument used was a Finnigan tracking GC-MS Analyzer (U.S. Finnigan Corporation).

The CSF-1A ultrasonic generator was a model from Shanghai (City, China) Ultrasonic Instrument Factory. The applied current was at 200 mA.

The spectrophotometer 752 UV was a model from Shanghai Analytical Instrument Factory.

The chloroform, carbon tetrachloride, tetrahydrofuran, ethanol and methanol were of analytical grade reagents from Tianjin Bodi Chemical Co., Ltd. production.

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Coconut-shell activated carbon was provided by Coconut-Island Environmental Protection Technology Co., Ltd. of Zhengzhou (Zhengzhou, city in China).

Experimental method and operation

Preparation of activated carbon: Through experimental and taking all factors considered into account, the optimum operation conditions were defined as follows.

Phenanthrene 0.0100 g was accurately weighed and placed into a 200 ml flask, the 100 ml hexane was added in to the flask. The solution was shaken for 10 minutes to fully dissolve the phenanthrene. The solution was placed for 20 minutes, and then its UV absorbance was measured by UV spectrophotometer.

Subsequently, the activated carbon of 0.5000 g was placed into the above flask. The flask was shaken for 10 minutes and then stored for 1 hour for filtration/adsorption (at room temperature). After adsorption, the clear liquid in flask was extracted; and its absorption determined by UV spectrophotometer.

The residual activated carbon, in which activated carbon had adsorbed phenanthrene, was placed into a vacuum dryer under nitrogen atmosphere at 25°C. In dryer under hexane was constantly eluted out, until activated carbon was the constant weight. And thus, the activated carbon was completely loaded with phenanthrene.

De-sorption of phenanthrene from activated carbon

Effects of different solvents on the de-sorption efficiency: The 0.5000g of activated carbon with adsorbed phenanthrene was weighed and placed into the flask, subsequently 100 ml of solvent was added. The solution was shaken for 1 hour and then stored for 1 hour at room temperature. The solution of 100 ml was taken out and measured by UV. The residual solution in the flask was dissolved with 100 ml solvent, then shaken for 1 hour and kept at rest for 1 hour, at room temperature. The above operation was repeated 5 times until a total solvent of 600 ml were used.

The different solvents including acetone, carbon tetrachloride, tetrahydrofuran, ethanol, distilled water were used, then the different de-sorption effects were determined.

The calculation formula of the de-sorption efficiency was as follows:

$$Des_{ef} (W\%) = ABS_{end} / ABS_{or} *100\%$$
(1)

In which Des_{ef} is the de-sorption efficiency; ABS_{end} and ABS_{or} are UV absorption values of final de-sorption solution and the solution of original phenanthrene, respectively.

It should be noted that the "original solution" is the solution

corresponding to 0.0100g phenanthrene used in preparation of activated carbon (adsorbing phenanthrene).

Effects of de-sorption time and manner on the de-sorption efficiency: Four activated carbons lots were prepared (paragraph 4.2.1) for de-sorption experiments, where each amount of activated carbon was loaded with same amounts of phenanthrene.

The experiments operation of de-sorption were the same as that described by previous section, and the total amount used solvent of every activated carbon was 1000 ml. One of the four runs was used with ultrasonic treatment; the ultrasound operation was repeated for 8 times every 0.5 hour.

De-sorption of fresh activated carbon: The fresh activated carbon is coconut shell type has never been used. In the de-sorption process, the sample amount is 20 grams and the de-sorption procedure was the same as the previous paragraph.

The procedure of using of ultrasonic vibration was repeated for 9 times. The total amount of solvent was 1000 ml. Finally, the solution was filtrated, and then remaining solution was placed in a vacuum system to remove the solvent. The residues (de-sorption substances) were analyzed by GC / MS.

The optimal analysis conditions of GC/MS: column was a DB-5MS, 30 meters long, 0.25 mm diameter, and 0.25 mm film thickness. Carrier gas helium of 1.0 ml / min, the initial temperature of 70°C for 3 minutes, then 10° C / min up rate, and finally heated to 250° C for 3 minutes. Electron impact was set at 70 electron volts (eV), atomic mass (amu) range was 30-350.

Results and Discussion

Adsorption efficiency of activated carbon with phenanthrene

By comparing the UV absorption of the original solution and the solution after adding activated carbon, the adsorption efficiency can be determined. The results of adsorption efficiency are listed in Table 1. With 5 runs as statistical base, the average adsorption efficiency was deduced to 99.91%, and the average value of adsorption capacity of AC is 20.22 (mg / g phenanthrene).

The result indicates that activated carbon has high adsorption ability, and phenanthrene can be easily loaded on activated carbon. Some related mechanisms were described simply as follows.

In PAH phenanthrene molecule, there are π bonds; While in there are π -bonds between carbon layers and there are carbonyl carbon, quinone-based, acid hydroxyl and other polar groups in carbon molecule [16,17].

When carbon molecules contact with phenanthrene molecular,

No	Concentration of phenanthrene g / 100ml	Absorption of solution 1 (UV 270nm)	Absorption of solution 2 (UV 270nm	Adsorption efficiency %	Adsorption capacity of AC mg/g
2	0.0102	0.9937	0.0011	99.889	20.377
3	0.0101	0.9925	0.0007	99.929	20.185
4	0.0100	0.9927	0.0006	99.939	19.987
5	0.0103	0.9931	0.0008	99.919	20.583
Average	0.0101	0.9930	0.0009	99.911	20.222

Table 1: Adsorption efficiency of phenanthrene on activated carbon

between π bonds, instantaneous dipole will be produced and further dispersion force will be produced. Polar molecule phenanthrene has "inherent dipole" being produce dipole moment forcer. In addition, through electric field of "intrinsic dipole", other polar and non polar molecules often produce new dipole named with as "induced dipole". The induced force would be generated from "induced dipole".

Above referred forces, which are including dispersion, induced force and dipole force, are not negligible, especially force derived from dipole. When two polar molecules (Philippines and activated carbon) close, the dipole will work. If poles are same then they would exclude each other; if two poles are different pole then they would attract each other. As different poles continually close to, two molecules continually also close to, finally this close to certain distance, the repulsion and gravitational achieve equilibrium and adsorption process is completed.

Due to Phenanthrene and activated carbon provide many dipoles and electron motion is fast, so the phenanthrene was easily and strongly adsorbed on carbon. And often non-pole solute can not to reach these.

De-Sorption of Phenanthrene on Activated Carbon

Effects of different solvents on the de-sorption efficiency: The different solvents including acetone, carbon tetrachloride, tetrahydrofuran, ethanol, distilled water were used at the same operation conditions, and with a total volume of 600 ml of solvent liquid, without ultrasound. The effects of different solvents on the desorption efficiency are shown in Figure 1.

To complete de-sorption of the phenanthrene, three factors are needed. The first, the solvent has capable to good solubility to phenanthrene; Second, the solvent molecules is smaller and then it easy penetrate and deep into the porous of carbon; Third, if polar functional groups (O =, -O-, -OH) has a high proportion in solvent, the de-sorption effect is more dominant. In the five de-sorption agent, the dissolved degree of aromatics in water is the worst of, therefore, the de-sorption efficiency is minimum with water.

Through handbooks and calculations, some basic data would be getting about other four organic solvents. The molecular weight of ethanol, acetone, tetrahydrofuran, carbon tetrachloride is successively 46.07, 58.08, 75.11, and 153.84 and their proportion of polar functional groups is successively 36.90, 27.55, 22.19, 0 (W%).

In our examples, de-sorption efficiencies of ethanol, acetone, tetrahydrofuran, carbon tetrachloride are successively are successively 40.011, 32.327, 11.942, 5.32

The changes characteristics of above three sets clearly reveal that the relationship of de-sorption effect of phenanthrene and property of solvent used follow a stringent law.

Effects of de-sorption time and manner : With the same desorption procedure (as mentioned in chapter 5.2.1), the 0.5000g of activated carbon with adsorbed phenanthrene of run1, run2 and run3 was weighed and placed into the flask, subsequently 100 ml of solvent was added. The solution was shaken for 1 hour and then stored for 1 hour (at room temperature). The solution was taken out and measured by UV. The residual solution in the flask was dissolved with 100 ml solvent. The above operation was repeated 9 times until a total solvent of 1000 ml were used. Every de-sorption efficiency was get from UV determination. The ultrasonic treatment was used in one (run4). The relations of de-sorption efficiency with the amount of solvent and ultrasonic are shown in Figure 2. In Figure X-axis represent ml amount of solvent used and Y-axis represent the recover rate namely de-sorption efficiency.

The results (Figure 2) clearly show that the de-sorption efficiency increases with the amount solvent. When ultrasonic treatment is used, the de-sorption efficiency is much higher than that of without ultrasonic. The maximum de-sorption efficiency is 91.40%. In addition, the de-sorption rate increased with increasing amount solvent used, however, after 900 ml used then showed a tendency of balance. The maximum volume applicable to maximum elution seems therefore to reach 900ml for the given amount of activated carbon.

After considering the results above and by taking all factors into account, the optimum process conditions were finally defined as follows: The amount of activated carbon: 0.5000g. The solvent used is ethanol, the total amount solvent used is 900 ml, and the ultrasonic treatment is used. This gives a desorption efficiency of >90%.

These experimental results also deeply imply that adsorption and de-sorption are reversible, but adsorption yields better efficiency than de-sorption; it is also the main reason that activated carbon is usually used as adsorbent.

De-Sorption of fresh activated carbon

The average content of total de-sorption of fresh active carbon is





measured to 0.043% (W %). It should be noted that an average value is obtained by 3 runs. By GC/MS analysis of de-sorption of active carbon, the total flow ion chromatogram of de-sorbed substances is shown in Figure 3. Typical MS qualitative comparison (m / z) is shown in Figure 4.

By qualitative analysis, the main organic extractions of de-sorption is 10-undecenoic acid methyl ester. It is clearly seen that the m / z of the chief de-sorption substance from activated carbon at 11.30 minutes of total flow ion chromatogram is almost the same as that of pure 10-undecenoic acid methyl ester. The characteristic values of m / z of pure 10-undecenoic acid methyl ester and the de-sorption substance



Note: The retention of composition (from AC) was 11.3min. (From Figure.3 Figure 3: The total flow ion chromatogram of de-sorption substance.





are mainly 15, 29, 41, 55, 59, 69, 74, 83, 87, 96, 110, 124, 149, 166. Thus the 10-undecenoic acid methyl ester in de-sorption substance is accurately defined with the qualitative matching of 93.3%. The structure of 10-undecenoic acid methyl ester is shown in Figure 5.

The results show also that the activated carbon is not absolute "pure" and nontoxic. These imply that activated carbon cannot be used as medicine or food additives.

Conclusion

A systematic study was carried out to characterize of adsorption and de-sorption of pure phenanthrene on activated carbon. The optimum de-sorption conditions are activated carbon 0.5000g containing phenanthrene, ethanol as extraction solvent, the total used amount of 1000 ml, with the ultrasonic treatment. The average value of highest de-sorption efficiency is 91.40%.

The results of de-sorption of fresh coconut shell-based activated carbon is that the average value of de-sorption efficiency is 0.043% (w %), and through GC / MS analysis the main substance from desorption was confirmed as 10-Undecenoic acid methyl ester.

These results show that "fresh" activated carbon is not absolutely pure and potentially toxic, underlining that it cannot be used as medicine or food additives.

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