Adsorption Analysis by Activated Carbon Derived from Nut Shells

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Abstract: Walnut, pistachio and chestnut shells are wonderful precursors for activated carbon. Due to the country's tremendous output and consumption of the nuts, a huge amount of nut shells are produced in China every year. In this study, activation temperature, activation time, impregnation ratio and zinc chloride activator concentration for high quality activated carbon formation are investigated experimentally by the methylene blue adsorption method. Copper ion adsorption is also analyzed. Chestnut shell is the most suitable material for activated carbon preparation. With 357mg/g methylene blue adsorption value, that is 2.6 times as the China's national standard. All three types activated carbon show the highest copper ion adsorption when the concentration of copper sulfate is 50ppm, and the maximum adsorption capacity is 1.06mg/g.

Keywords: Activated carbon, Zinc chloride, Nut shell, Copper sulfate, Methylene blue

1. Introduction

According to the China Statistical Yearbook, walnut plantation area in China was 1.667million square hectares with about 0.21 billion walnut trees, and the yield of walnut was 5 hundred thousand tons in 2006; it ranked the first in the world[1]. The walnut shell takes about half of the weight of the walnut; waste disposal problem are created when these shells are thrown out. Xie et al. find that walnut shells are good raw material for activated carbon production due to the relatively high carbon content and less ash production[2].

Similar with walnut, the production of Chinese chestnut in 2009 was 1.62million tons, taking up 76.5% of world production, ranking first in the world for decades[3]. Large numbers of chestnut shells have been discarded, burnt and decomposed; polluting the environment and causing fire. Chestnut shells, containing 34.35% carbon and 6.5% ash , are rich renewable carbon resources. Chen et al. also reported that the chestnut shell activated by zinc chloride with 0.04~0.14cm^3/g of average pore total volume and above 1500m^2/g of the specific surface area. Chestnut was also a suitable material to produce activated carbon[4].

In addition, pistachio is a kind of popular snack in China due to the rich in vitamin, fiber and mineral elements, but low in fat and calorie. According to the Iran Daily, the Chinese have been the top pistachio consumers worldwide with an annual consumption of 80,000 tons[5]. From 2005 to 2008, China produced 34,000ton, 36,000ton, 38,000ton and 40,000ton; rank the fourth of the world[6]. However, there is no related research about pistachio shell activated carbon, and this project wanted to study the potential ability for pistachio shell activated carbon production.

The above three shells are the suitable raw materials for activated carbon production. If the huge waste of these shells have been reused, it will not only reduce the land space for landfill and the waste of resource, but also recycle the solid waste material for environmental pollution treatment.

2. Methodology

In the experience, the waste material walnut shell, pistachio shell and chestnut shell are chosen as the raw material, and zinc chloride is used as activator for activated carbon production. The method is based on the Study on Preparation on Activated Carbon from Excess Activated Sludge and its Application: the optimum preparation conditions were set by activation temperature 550℃, time of activation 60min, concentration of ZnCl2 40%, the ratio of solid to liquid 1:2. So the impregnation ratio gradient of material to activator has been set up: 1:1.5, 1:2, 1:2.5 and 1:3. The ZnCl2 concentration gradient was: 10%, 20%, 30% and 40%. The activation temperature was: 350℃, 450℃, 550℃, 650℃. While the activation time gradient was: 30min, 60min, 90min and 120min. The absorbability of the activated carbon was determined by methylene blue adsorption. The method is based on the GB/T 12496.10-1999 (Test method of wooden activated carbon—determination of methylene blue adsorption).

After the suitable conditions were determined, the good adsorbed activated carbons were found, then the researcher processed to use these kinds of activated carbons to study the copper ion adsorbed capacity.

3. Result

For the best activation temperature determination, the temperature gradient was set: 350, 450, 550 and 650℃, while the other conditions were the same. Activation time was 60min, concentration of ZnCl2 was 40%, and the ratio of solid to liquid was 1:2. According to this method, and for the best activation time determination, the time gradient was set: 30, 60, 90 and 120min, while the other conditions were the same. Temperature of activation was 550℃, concentration of ZnCl2 was 40%, and the ratio of solid to liquid was 1:2. According to this method. Besides, for the best activator concentration determination, the concentration gradient was set: 10%, 20%, 30% and 40%, while the other conditions were the same. Temperature of activation was 550℃, time of activation was 60min, and the ratio of solid to liquid was 1:2. Yields and methylene blue adsorption influenced by impregnation ratio.

For the best impregnation ratio determination, the impregnation ratio gradient was set: 1:1.5, 1:2, 1:2.5 and 1:3, while the other conditions were the same. Temperature of activation was 550℃, time of activation was 60min, and the concentration of the zinc chloride was 40%.

Three types of the raw materials have been used to do the parallel tests which produce activated carbon by each group of the condition respectively. For Type 1, the activation temperature was 550℃, activation time was 90min, activator concentration was 30% and the impregnation ratio was 1:2.5. For Type 2, the activation temperature was 450℃, activation time was 30min, activator concentration was 40% and the impregnation ratio was 1:3. For Type 3, the activation temperature was 550℃, activation time was 60min, activator concentration was 40% and the impregnation ratio was 1:3.

All activated carbon produced from the parallel test has used for copper ion adsorption. The best copper ion concentration was been found in the pretest whose copper ion concentration was set (20ppm, 50ppm and 100ppm). Under this concentration, the copper ion adsorption by the activated carbon from the parallel test and brought from the market have been studied

4. Discussion

The yield of the activated carbon, ranging from 41.09% to 66.85%, decreases with the increasing activation temperature according to the results. The weight of activated carbon gains declined dramatically when temperature between 350 and 550℃, while it decreases slightly after 550℃. Yuan et al. (2010)7 points out that, because of the increasing carbon loss with the raising temperature, the productivity of activated carbon decreased with the increasing temperature. According to the previous study, pyrolytic reaction for activated carbon constituted depolymerization and polycondensation reaction. The previous reactions were mainly depolymerization, decomposition and deaeration, which produced a large number of volatile substance. With the increase of time, the volatile substances increased, so the solid material remain less. When most of the volatile substances have been separated, some macromolecule thermalized to micromolecule even gases, and some micromolecule polymerized into macromolecule. Meanwhile, small part would go through polycondensation. During this period, the weight would decrease slowly.

Compared to yield and different raw material, the chestnut shell base activated carbon is produced most rage from 50.59% to 66.85%, while pistachio shell produces less in the same activation temperature range from 41.09% to 54.18%. It shows that, chestnut shell produces more activated carbon than that of walnut shell and pistachio in the same activated condition.

The yield of the same raw material base activated carbon is no obvious change with the increasing activation time except the activated carbon producing at 90min, which the walnut shell activated carbon ranges from 46% to 48%, pistachio shell of that ranges from 42%to 44% and chestnut shell ranges from 49% to 51%. Besides, chestnut shell produces most activated carbon while pistachio produced less at the same condition. However, suddenly high yield happens when the activation time is 90min. It may be due to some errors during the experiment that cause the high yield, or 90min is the optimum time for shell base activated carbon production.

The result of the methylene blue adsorption indicates the best activation time for walnut, pistachio and chestnut shell activated carbon processing is 90min, 30min and 60min respectively; and the amount of methylene blue adsorbed is 125.02mg/g, 160.74mg/g and 178.60mg/g respectively. For walnut shell activated carbon, the methylene blue adsorption starts to rise at 60min, then reaches and stays at the point of 125.02mg/g. However, for pistachio shell, it continually fells between 30 to 20min. In addition, the adsorption of chestnut shell activated carbon firstly increases and reaches a crest at 60min, then drops to and keeps stable at the point of 125.02mg/g. The carbonized raw material have not been activated completely and the methylene blue adsorption increased with the time increases to reached the zenith at the previous of heating, but if the activation lasts for long time, the micro pore form by the reaction between carbon skeleton and oxygen will become mesopore or Marco pore, as a result the specific area and the value of methylene blue adsorption decreases.

The methylene blue adsorption built up with the increasing zinc chloride concentration, except the walnut shell has little drop when the concentration was 40%. The optimum zinc chloride concentrations for both pistachio and chestnut shell activated carbon are 40%, while 30% for walnut shell. It is generally accepts that, zinc chloride is a dehydrogenating agent which creates the hole by promoting the dehydrogenation and aromatization of the cellulose during the activated process. Besides, the zinc chloride can prevent the formation of tar. Thus, the pore structure will be formed after zinc chloride has been washed away[8]. The higher concentration, the more zinc chloride and the stronger function, so larger value of the methylene blue adsorption can be observed.

However, the methylene blue adsorptions for all of them increase slowly with the increasing impregnation ratio. The maximum adsorption for both pistachio and chestnut shell activated carbon achieve when it immersed in 1:3 zinc chloride solution, but 1:2.5 was for Walnut shell. The influence of impregnation ratio is similar to the influence of zinc chloride concentration, while higher ratio means more chloride in solution before the adsorption reaching the maximum value.

5. Conclusion

Due to the results of pretreatment, chestnut shell is the most suitable material for producing activated carbon compared to other shells with higher yield and the optimum methylene adsorption. According to the prior study, the best impregnation ratio, the activator concentration (zinc chloride concentration), activation time and activation temperature for walnut, pistachio and chestnut shell activated carbon is 1:2.5, 1:3, 1:3, 30%, 40%, 40%, 90min, 30min, 60min, 550℃, 450℃ and 550℃ respectively. Under these improved method, all methylene blue adsorptions of three types activated carbons have exceed the first grade of the national standard, which is 135mg/g. Chestnut shell activated carbon shows 2.6 times higher adsorption capacity than the national standard. It means that these activated carbons could represent good adsorbility for macromolecule. Certain copper ion adsorbility can be found in all activated carbons provided from the parallel test when the copper sulfate concentration is 50ppm, but it is lower than the commercial activated carbon. According to the FT-IR result, both pistachio and chestnut shell activated carbons have certain functional groups such as C=O and C-O-C, contributing to the adsorption capicity. However, to improve the copper ion adsorption, further study is needed such as activated carbon modification by some special chemicals.

Reference

1. National Bureau of Statistics of China. China statistical yearbook 2007. Retrieved 2014 Sept 22 from http://www.stats.gov.cn/.
2. Xie R, Wang H, Chen Y, *et al*. Walnut shell-based activated carbon with excellent copper (II) adsorption and lower chromium (VI) removal prepared by acid-base modification. Environmental Progress & Sustainable Energy 2013; 32(3): 688-696.
3. Chinese Economic Forest Association. Current development of chestnut in China 2012. Retrieved on 2014 Sept 4 from http://www.forestry.gov.cn/portal/jlxh/s/3501/content-549851.html
4. Chen C, Ren Q, Xu Q, *et al*. Adsorption of heavy ion by chestnut shell activated carbon 2014 (in Chinese). Ion Exchange and Adsorption 2014; 30(1): 029-038.
5. Dehqan S. Pistachio exports to hit record. Iran Daily 2010 May 13. Retrieved on 2014 Sept 22 from http://old.iran-daily.com/1389/3/2/MainPaper/3686/Page/4/Index.htm#.
6. Food and Agriculture Organization. Food and agricultural commodities production 2011. Retrieved on 2014 September 22from http://faostat.fao.org/site/339/default.aspx.
7. Yuan S, Zhu Y, Liang M. Preparation of activated carbon from grapefruit bran by activation with Zinc Chloride (in Chinese). Environmental Science & Technology2010; 33(6E): 22-25.
8. Yi S, Wang X, Li N, *et al*. Research process in activation treatment technology of activated carbon (in Chinese). Material Review2008; 22(3): 72-75.