Characterization of Activated Carbon Prepared from Aegina Pistachio Shells for Hg Removal

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Abstract

Preparation of activated carbon from agricultural bio-products is a promising way to produce useful adsorbents for Hg removal. In this study Aegina pistachio shells were used as raw materials and the activation was carried out by impregnation with $ZnCl_2$ and heating at 750°C under N_2 atmosphere. Three different levels of impregnation ratios (IR) were used for the chemical activation procedure, i.e. IR 1.0, 1.5 and 2.0 grams of $ZnCl_2$ per gram of raw material. Further sulfurization treatment of the chemically activated carbons was also examined as a means to improve the adsorption capacity of activated carbons toward Hg. Overall six different types of activated carbons were produced and characterized regarding their physicochemical properties and their capacity to adsorb mercury. The specific surface area was determined by the BET method. The amount of acidic and basic function groups was determined with Boehm method and the surface chemical characteristics of activated carbons were investigated using the FT-IR spectroscopic method. Preliminary Hg adsorption experiments indicated that the sulfur modified carbons were much more efficient for the removal of Hg from aqueous streams compared to simple chemically activated carbons.

Keywords: activated carbon, sulfur modification, characterization, mercury adsorption

1. Introduction

According to the Global Merury Assesement 2018 of UN Programme the total estimated inventory of anthropogenic mercury releases is about 580 tonnes per year, without including artisanal and small-scale gold mining. Artisanal and small-scale gold mining imported about 1220 tonnes of mercury into the terrestrial and fresh water environments in 2015. Hence, it is mandatory to remove Hg (II) from wastewaters before they are released into the environment. Activated carbon is a remarkable porous material, with large specific surface area, which is useful for adsorption in aqueous streams. As environmental pollution is becoming more more a tough problem, the need for activated carbon is growing. Various materials are used to produce activated carbon and some of the most commonly used are agriculture wastes such as date palm, coirpith, sago waste, furfural, fertilizer waste, etc. (Ioannidou and Zabaniotou 2007). In this research Aegina's pistachio shells were used to prepare activated carbon in granular form (GAC). Due to the high affinity of Hg with sulfur, part of the synthesized GAC products were subjected to additional treatment with a sulfur agent. Both simple and S-modified GACs were evaluated for their capacity to remove Hg from aqueous solutions.

2. Materials and Methods

The raw material used for the synthesis of granular activated carbon (GAC) was pistachio shells from Aegina Island. The shells were crushed and sieved to obtain particulates with size 0.8-1.0 mm. The synthesis of GAC was carried out applying the chemical activation methodology and using $ZnCl_2$ as dehydration agent. The impregnation solution was prepared by dissolving 50, 75 or 100 grams of $ZnCl_2$ in 250 mL of deionized water and was mixed with 50 grams of crushed shells. The mixture was agitated at 60°C for 3 hours, and then filtered and the impregnated shell particles were dried at 100°C for 24 hours and then transferred in an oven for thermal treatment at 750°C for 2 hours under a N_2 flow. Some samples of the chemically activated carbons were subjected to a sulfur modification treatment, which involved mixing of the GAC with a Na_2S solution and an additional thermal treatment step. The details are given in Karagianni et al. (2018).

Elemental analysis of the raw material and the activated carbon products was carried out by LARCO GMMSA using a CHNS Analyzer. The specific surface area and the porosity of the obtained activated carbons was determined by N_2 adsorption at -200 °C by BET measurements using a Quantachrome NOVA 1200 analyzer. The IR spectra of the samples were recorded using a Perkin Elmer 1100 series FT-IR model operating in the range 4000–400 cm^{-1}. The amounts of acidic and basic functional groups were determined by the Boehm method.

The Hg adsorption tests were carried out mixing 500 mL of a 60 mg/L Hg solution with 0.5 g of simple GAC or 0.2 g of sulfur modified carbon, GAC-S. The experiments were carried out at pH 6. The mixtures were agitated at 200 rpm for 3 h at room temperature and then the activated carbon was separated by filtration and the concentration of Hg in the aqueous solution was determined by the Rhodamine 6G method.

3. Results

The main characteristics of raw material and GAC products are presented in Table 1. The sulfur content of the examined solids decreased from 0.14% in the dried pistachio shells to about 0.02% in the three activated carbons (GAC) regardless of the IR used. After the sulfurization treatment, the sulfur content was 1.91% in GAC with IR=1, and decreased to 1.41% and 0.91% in the CAC-1.5 and GAC-2 respectively. The specific surface area as measured by BET was found to increase with the applied IR during the activation of carbon, from 711 m^2/g at IR=1 up to 887 m^2/g at IR=2. After the sulfurization treatment the BET surface increased for S-GAC sample with IR=1 (from 711 to 811 m^2/g), but decreased for the S-GAC samples with IR 1.5 and 2. The amount of acidic groups in the simple GAC was found to range between 1.20 and 1.35 meq/g. In the sulfur modified samples the content of acidic groups decreased from 1.22 meq/g to 0.17 meq/g, as the IR increased from 1 to 2. The amount of basic groups in the simple GAC was low, in the range 0.01-0.13 meq/g, but increased after the sulfurization treatment and varied between 0.59 and 0.96 meq/g.

Table 1. Characteristics of raw materials and activated carbon

	Raw mat.	GAC-1	GAC-1.5	GAC-2	S-GAC-1	S-GAC-1.5	S-GAC-2
C%	40.9	77.7	79.0	81.8	64.1	64.7	70.3
H%	6.08	1.93	1.43	1.67	1.52	2.33	2.41
N%	0.59	0.14	0.30	0.22	0.30	0.18	0.21
S%	0.14	0.025	0.023	0.025	1.91	1.41	0.97
BET (m^2/g)		711	736	887	811	673	683
Acidic gr. (meq/g)		1.35	1.20	1.33	1.22	0.64	0.17
Basic gr. (meq/g)		0.13	0.01	0.02	0.59	0.63	0.96
Ads. (mgHg/g)		21.8	17.2	21.7	40.5	44.2	62.2

The FTIR spectra of simple and sulfur modified GAC samples produced with IR=1 are compared at Figure 1. A very characteristic sharp band appears at 1383 cm^{-1}. This band was also observed by Li et al. (2014) in a commercial activared carbon product and was attributed to ν(C-H) stretching vibration. The bands at 1695 and 1622 cm^{-1} are attributed to ν(C=O) vibrations corresponding to carboxylic and carbonyl groups respectively. The broad shoulder at 1113-1129 cm^{-1} at GAC-1 sample can be ascribed at C-O vibrations of alcool groups and the band at 613cm^{-1} coresponds to the out of plane bending vibration $\gamma(O-H)$ (Chong Lua and Yang, 2005). The two bands at 1225 and 1113 cm^{-1} appear with stronger intensity in the S-modified sample S-GAC-1 and according to Hampton et al. (2018) can be attributed to the formation of C=S and S=O bonds. The adsorption of Hg by the six GAC samples is shown in Figure 2. As seen in the figure the uptake of Hg on the simple GAC samples ranges between 17 and 22 mg/g, without any apparent effect of the impregnation ratio used during the chemical activation. The uptake is clearly improved after sulfurization, with values varying between 40 and 62 mg/g. The highest Hg adsorption was observed in the S-GAC-2 sample, containing the highest amount of basic groups, despite the fact that the sulfur content was lower in comparison with the other sulfurized samples. It is known that Hg(II) species have a strong electrophile character. This fact can explain the observed affinity of Hg with the basic groups of S-GAC-2 sample.

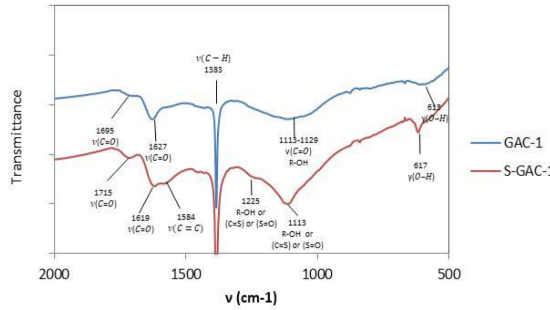

Figure 1. FTIR spectra of simple and sulfur modified GAC samples produced with IR=1

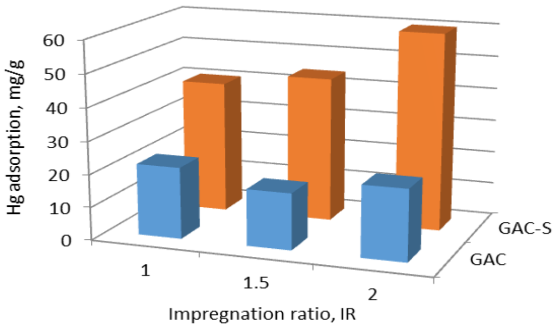

Figure 2. Adsorption of mercury by the simple and sulfur modified GAC samples.

4. Conclusions

Aegina pistachio shells were used for the synthesis of simple and S- modified GAC products. The sulfurization treatment caused the decrease of BET surface area and the increase of the amount of basic functional groups. As far as Hg(II) adsorption is concerned the S-modified GAC products were found to be more efficient, due to the electrophile character of Hg(II) and their chemical affinity for sulfur.

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