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Investigation of Mercury Vapor Treatment by Activated Carbon Made from Coconut Shell and Denatured by Elemental Bromine

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Abstract

Coconut shell activated carbon of TraVinhcompany, Vietnam was oxidized by bromine solution at pH 4-6 in normal temperature and pressure. The efficiency of bromine carried on AC surface reached 70.95 to 98.50%. The IR spectrum showed that in surface of the brominated AC appeared C-Br, carbonyl and carboxyl groups. The adsorption capacity of brominated AC reached more than 130 mg/g at 40^{o}C and mercury concentration around 32 mg/m^{3}. The mercury vapor adsorption of the material was almost uninfluenced by experimental temperature. Used brominated AC can be regenerated and recovered mercury metal. The regenerated material has adsorption capacity of 86.92% in comparison with initial material and weight loss was 6.23% at laboratory scale examination.

Keyword:brominated activated carbon; mercury vapor adsorption

1. Introduction

Mercury is one of most toxic metals, easy evaporate and transfer in the air. According to UNEP report 2013, the mercury emission was increased every day past and anthropogenic emission was many times more than it's from geo-sphere (UNEP, 2013). The global emission of mercury to the air from anthropogenic sources is estimated as 1960 tones in 2010. Despite recent progress in improving the available knowledge base, the emissions estimate still has large associated uncertainties, giving a range of 1,010-4,070 tones. Current anthropogenic sources are responsible for about 30% of annual emissions of mercury to air. Another 10% comes from natural geological sources, and the rest (60%) is from 're-emissions' of previously released mercury that has built up over decades and centuries in surface soils and oceans. The anthropogenic emissions are accounting for burning of fossil fuels and solid waste, production and treatment of fluorescent lamps and LCD monitors, chlorine production, gold extraction and other activities (Driscoll *et al*., 2013). According to US EPA statistics, the sources of mercury emission is countdown as 31.0% from thermoelectric power plants, 18.5% and 11.0% from municipal and hospital waste incinerators, 5.6% and 3.0% from chlorine and cement production and other activities contributed 31.0% (Johnson, 2001; US EPA, 1997). It sounds that, increasing industrialization has made Asia the main source region of mercury emissions to air, with East and Southeast Asia accounting for about 40% of the global total, and South Asia for a further 8% (UNEP, 2013). The global emission of Hg projected to 2020 was concerned (Pacyna *et al*., 2010).

These data above issue a challenge to scientists and technologists to eliminate concentration of mercury in exhaust gases to minimum before it's emitted to the air. The mercury vapor can be adsorbed on various adsorbents; but among them, activated carbon impregnated sulfur and halogens were mostly used. Ozaki *et al*. (2008) used H2S as sulfur source for sulphurization of activated carbon (AC) impregnated iron(III) at deferent temperature to formed adsorbent which has adsorption capacity higher than sulphurated simple AC (Ozaki *et al*., 2008). Feng *et al*. (2006). modified AC fiber by H2S to get material with high adsorption capacity of mercury vapor. Elemental sulfur was also used for sulphurization of AC and other porous materials. The mercury vapor adsorbed on AC-S materials is allowing both physical and chemical adsorption mechanism. The investigation of Yang *et al*., 2007 showed that increase of temperature the physical adsorption decreased, but chemical adsorption increased. Halogenated AC was commonly used for mercury vapor treatment. Matsumura (1974) investigated adsorption capacity of oxidized AC to obtained value of 14.3 mg/g and of iodinated AC this value was 47.8 to 108.0 mg/g at 30^{o}C and mercury vapor concentration of 38 mg/m^{3}. Liu *et al*. (2007) used bromine vapor injected to exhaust gas from coal electric power plant to enhanced efficiency of Hg vapor removal to more than 90% and reduced amount of adsorbent from 10-20 lb to 5lb per a million cubic meter gases in comparison with only fly ash (Liu *et al*.,

2007). In their report, Hutson *et al*. (2007) demonstrated the bromine binding on AC surface is reason to increase Hg vapor adsorption by strong bond of Hg and Br.

In this paper, we used elemental bromine as oxidation and bromination reagent for bromine modification of TraBac (Vietnam) coconut shell AC and studied its adsorption capacity of Hg vapor in laboratory scale. The regeneration of used material and mercury recovery were also investigated.

2. Materials and Methods

2.1. Bromination of TraBac coconut shell AC

Granule AC with diameter of 0.5-1.0 mm was firstly washed by deionized water to pH around 7 and dried for 4 hours at 100 -110°C. After cooling naturally, AC was soaked in bromine solution with Br/AC ratio of 1; 3; 5; 7; 9 and 12% (w/w) for 1 to 8 hours at normal temperature and pressure. Soaking time passed, the solution was removed, the solid material was washed by deionized water and dried in the same condition as before. The bromide and remained bromine in the solution were analyzed (APHA, 1995) and amount of bromine held on to AC ($m_{Br\text{-}AC}$) was calculated by following formula:

$$m_{Br\text{-}AC} = m_o - (m_{Br\text{-}} + m_{Br2})$$

Where m_o is initial bromine amount; $m_{Br\text{-}}$ is bromide amount remained in solution; m_{Br2} is amount of bromine remained in solution after soaking time.

2.2. Determination of Hg vapor capture possibility of the AC-Br material

The determination was carried out at mercury vapor adsorption equipment described in Fig. 1.

Mercury adsorption study were conducted with 0.5 g of adsorbent mixed with 5.0 g of quartz sand having the same particles size (0.5-1.0 mm) filled in adsorption column and carried out in thermostat room. Mercury vapor was saturated at designed temperature in evaporator basin, diluted and carried by clean air passed through the adsorption column with suitable flow rate. The inlet mercury concentration was controlled by adjusting the air mixing ratio and kept constantly around 32 mg/m^3 for studies at different temperature. The Hg vapor in effluent stream was absorbed in absorption tubes containing solution of $KMnO_4$ in HNO_3 and analyzed by AAS connected with cool vapor generator. Adsorption time was 60 min for all examinations. The mercury vapor capture possibility of the materials was quantified by a comparison between the Hg contents before and after adsorption.

2.3. Determination of dynamic equilibrium adsorption capacity

The dynamic adsorption of mercury vapor by AC-Br was conducted on the apparatus described in Fig. 1 with the same examination conditions presented above. The adsorption process was carried out continuously. The average concentration of mercury of every fraction of two hours adsorption (equal 120 L gas passed) was determined. The examination was continued until the mercury concentration in the effluent almost equal the inlet concentration. The dynamic equilibrium adsorption capacity of the material was calculated by following formula:

$$q = \frac{C_o.t_T.w - \Sigma_1^n C_i.t_i.w}{m}, \left(\frac{mg}{g}\right)$$

Where C_o is inlet Hg concentration (mg/m^3), C_i is Hg concentration in fraction i (mg/m^3), t_T is total adsorption time (min), tiis the time of 1 fraction (min), w is flow rate (L/min) and m is material quantity (g).

2.4. Material regeneration and mercury recovery

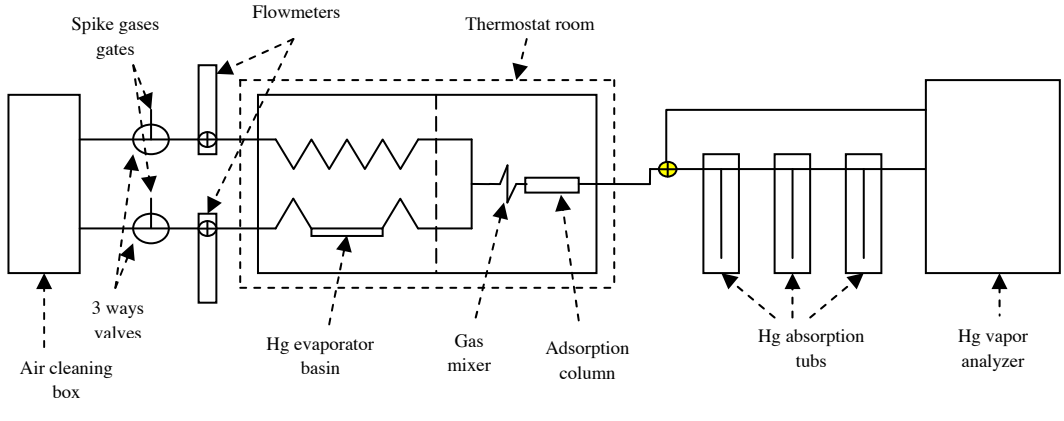

Figure 1. The schema of the Hg vapor adsorption study equipment

Table 1. Bromination efficiency

Materials	m_0 (g)	m_{Br-} (g)	m_{Br2} (g)	m_{Br-AC} (g)	Efficiency (%)
AC-Br-1	1.000	0.015	< 0.001	0.985	98.500
AC-Br-3	3.000	0.086	< 0.001	2.614	97.133
AC-Br-5	5.000	0.325	< 0.001	4.675	93.500
AC-Br-7	7.000	0.543	< 0.001	6.245	89.214
AC-Br-9	9.000	1.237	< 0.001	8.560	84.044
AC-Br-12	12.000	2.328	1.158	9.672	70.950

Note: m_0: initial bromine amount, m_{Br-} and m_{Br2}: bromide and bromine amount remained in soaking solution, m_{Br-AC}: bromine amount staying on AC surface.

Mercury desorption and material regeneration were carried out in both batch and column continual operations. In batch desorption study, the used adsorbent AC-Br was washed by oxidative solution of $KMnO_4$ dissolved in HNO_3 with liquid/solid ratio of 10 ml/1 gram. After soaking time of 3 hours, amount of mercury in the solution fraction was analyzed and the process was repeated until mercury in last fraction was undetected.

In column continual desorption operation, the used adsorbent was filled in the stripping column of 12.5 mm diameter and the washing agent (as the same solution using for batch operation) was passed through the column at a flow rate of 0.5 ml/min.cm^2. Concentration of mercury in every 10 ml effluent fraction was determined by AAS with cool vapor generator. The column desorption study was completed when mercury concentration in last fraction was almost zero.

After regeneration, the mercury metal was recovered by zinc powder in acidic solution. The adsorption material was washed by water to free all soluble substances and dried at 100-110^{o}C for 4 hours. The dynamic adsorption of regenerated material was restudied in the same experimental conditions as described above and compared with that of the initial AC-Br.

3. Results and Discussion

3.1. Optimization of AC bromination

3.1.1. Effect of Br/AC ratio on AC bromination

Brominated AC materials signed as AC-Br-1 to AC-Br-12 are corresponding with Br/AC ratio 1.0 to 12.0% in bromination process. In the same conditions as presented in section 2.1, the bromination was carried out with 100.0 g AC and soaking time of 180 min, obtained results are showed in Table 1.

According to data on Table 1, when Br/AC ratio increased, the bromination efficiency decreased but amount of bromine stayed on AC keeping increased; and when the Br/AC ratio reached to 12.0%, appeared elemental bromine remained in the solution. This means, at Br/AC ratio of 12.0%, all reductive groups on AC surface which have red/ox potential lower than oxidation potential of Br_2/Br^- pair, were oxidized. During bromination, there occurred parallel two processes, oxidation and binding of bromine with carbon atoms and functional groups on AC surface. Those showed in IR spectrum both variations, 500 cm^{-1} characterized for C-Br bond and 1,600-1,780 cm^{-1} characterized for oxidized groups as carbonyl and carboxyl (as showed at Fig. 2).

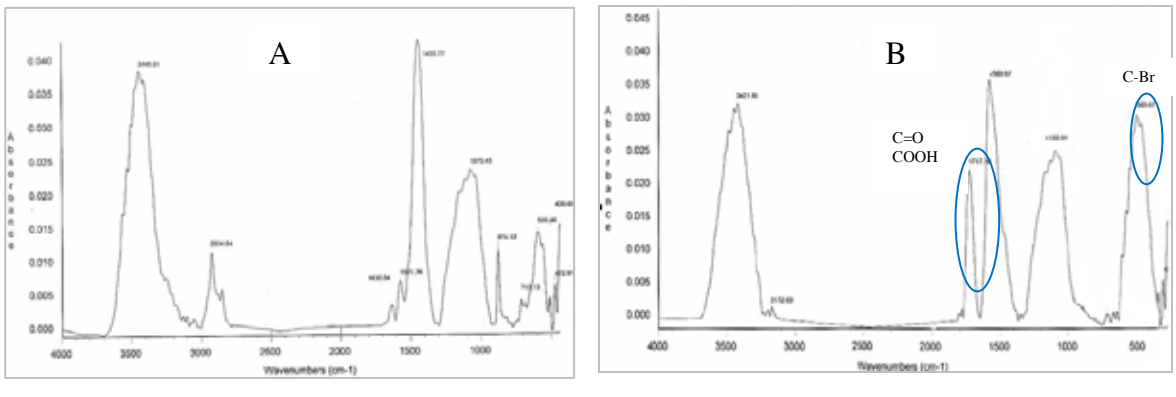

Figure 2. IR diagrams of AC (A) and AC-Br (B)

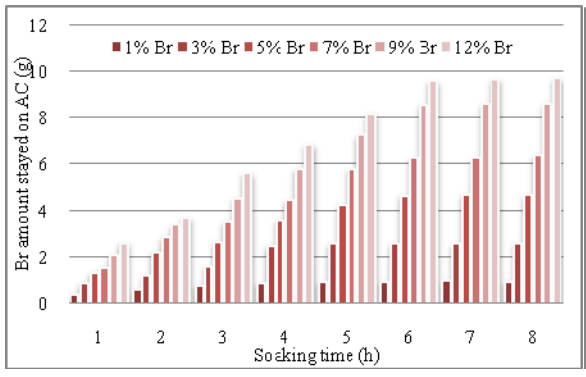

Figure 3. Effect of soaking time on bromination efficiency

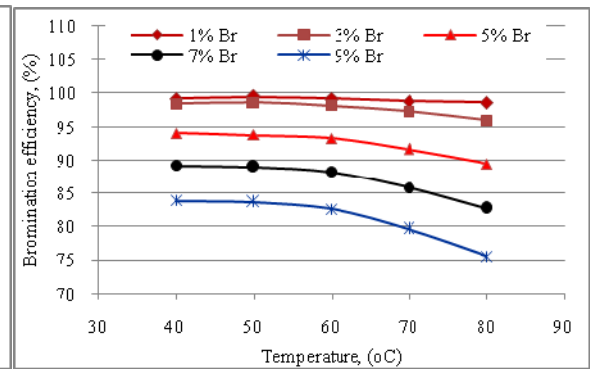

Figure 4. Effect of temperature on bromination efficiency

Since AC surface was oxidized and there appeared new bonds between bromine and carbon on AC surface, so specific surface area of AC was reduced, average pore diameter was increased and pore volume was also increased (as showed in Table 2).

3.1.2. Effect of soaking time and temperature on bromination efficiency

Due to the high porosity of AC and sufficient time for oxidation reactions and bromine binding on AC surface, so contact time of two phases prolonged. At lower Br/AC ratio (1 to 3%), the phase contact time was about 4 hours, the reactions were almost reached equilibrium state; but at higher ratio, the equilibrating time was about 6 hours (as showed in Fig. 3).

The influence of temperature on bromination efficiency is showed in Fig. 4. It is clearly that, the increase of temperature, the decrease of bromination efficiency. This influence is quite weak in lower bromine concentration but stronger in higher concentration. The reason of this phenomenon can be the first was, at high temperature, especially in the case of higher bromine concentration, red/ox reaction occurred more furiously, a huge amount of bromide ion was produced simultaneously, but not all of them can be linked on AC surface, and the second was escape of bromine from soaking solution, the higher temperature, the more bromine evaporated.

3.1.3. Effect of pH on bromination efficiency

In bromination process, the initial pH of bromine solution strongly influence on bromination efficiency, especially when it overcomes neutral value (as showed in Fig. 5). The reason is, in the acidic condition, bromine oxidized AC surface directly; but in neutral and alkaline condition, bromine reacts with water to change to bromide and hypobromite ions, which have lower oxidation potential, so its oxidation ability reduced and result in bromination efficiency also reduced.

From obtained investigation results, the optimal conditions for bromination of TraBac AC are the ratio of Br/AC is not exceeded 9%, the soaking time must be at least 6 hours, the reaction temperature is rather lower than 50°C (initial temperature lower than 30°C) and initial pH value is in the range of 4 to 6.

3.2. The Hg vapor capture possibility of AC-Br

Investigation of Hg vapor capture possibility was carried out by the way as presented in section 2.2. with

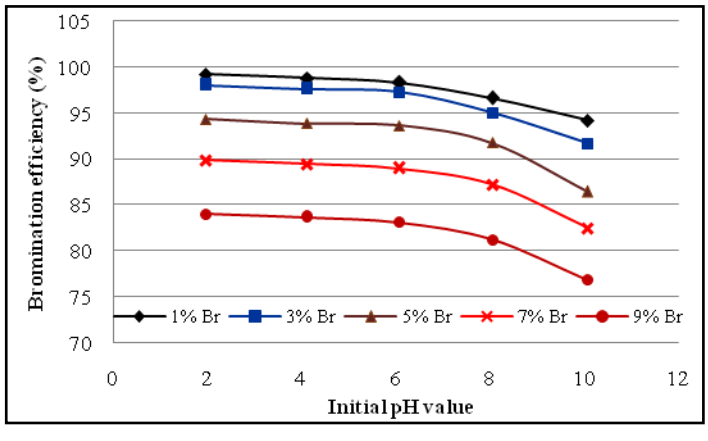

Figure 5. Effect of pH on bromination efficiency

Table 3. Hg vapor capture possibility of AC and AC-Br at different temperature

Temperature, (°C)	Hg vapor capture possibility, (%)						
	AC	AC-Br-1	AC-Br-3	AC-Br-5	AC-Br-7	AC-Br-9	AC-Br-12
30	72.5	95.7	98.4	99.2	99.2	98.9	99.2
40	70.1	95.5	98.3	99.2	99.2	99.2	99.3
50	67.7	95.2	98.1	99.4	99.2	99.2	99.4
60	62.7	94.9	97.9	99.0	99.4	99.5	99.4
70	55.4	94.1	97.4	99.4	99.6	99.6	99.5
80	42.2	93.5	97.3	99.4	99.7	99.6	99.7
90	28.1	92.8	97.1	99.5	99.7	99.5	99.7

inlet Hg vapor concentration of 32.267 mg/m^3, gas flow rate of 1.0 L/min.cm^2 and temperature from 30 to 90°C. The investigation results are showed in Table 3.

According to data presented in Table 3, adsorption temperature significantly influenced on Hg vapor capture on original AC. Adsorption temperature increased from 30 to 90°C, the capture possibility decreased from 72.5% to 28.1%. And this phenomenon still appeared in the cases of AC-Br with lower Br/AC ratio and lightened from 1% to 3%. But when Br/AC ratio is 5% and higher, the capture possibility has trend to increase when adsorption temperature increased. This phenomenon appeared because of the adsorption mechanism of Hg vapor on original AC surface is predominantly physical, which is strongly influenced by temperature. When the AC surface is brominated, the Hg vapor was held on AC mainly by chemical binding between Hg and Br. So increase of temperature supported reaction of Hg with Br binding on AC surface. On the other hand, Hg-Br bond is strong enough to confront temperature increasing. This is very important property of AC-Br adsorbent in application for Hg vapor treatment in stack gas.

3.3. Dynamic adsorption equilibrium of Hg vapor on AC-Br

Due to temperature almost uninfluenced on AC-Br with low Br/AC ratio and positively effected on adsorption of Hg vapor on AC-Br with Br/AC ratio higher than 3%, therefore this investigation was carried out following the procedure presented in section 2.3 and at 30°C with Hg vapor concentration of 32.267 mg/m^3, and gas flow rate of 1.0 L/min.cm^2. The investigation result is shown in Fig. 6.

According to Fig. 6, until to fraction 15th, the concentration of Hg vapor in effluent gas stream scarcely appeared with remarkable value and in faction 21st, outlet Hg concentration almost equal inlet concentration. And dynamic equilibrium adsorption capacity of Hg vapor on AC-Br-5 was 132.524 mg/g (calculated following equation in section 2.3). Dynamic equilibrium adsorption capacity of other AC-Br materials were studied by the same way as for AC-Br-5. The results are presented in Table 4.

According to data in Table 4, in the same experimental conditions, the dynamic equilibrium adsorption

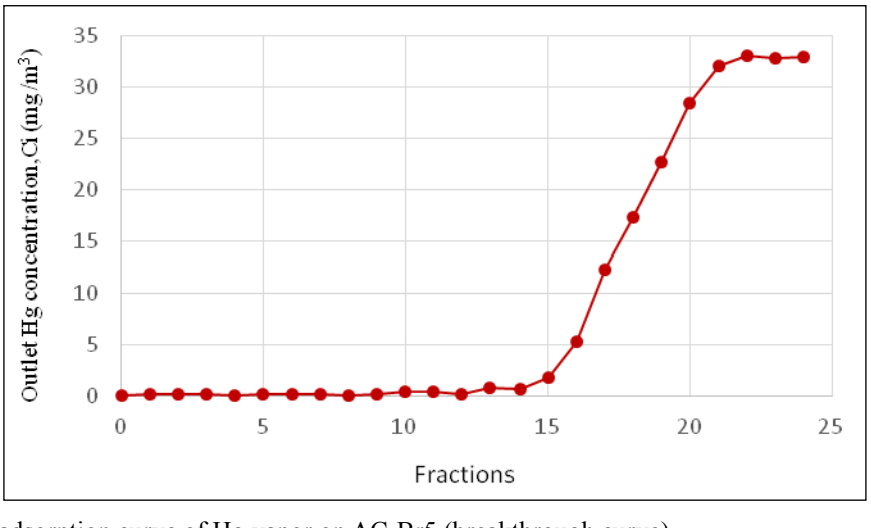

Figure 6. Dynamic adsorption curve of Hg vapor on AC-Br5 (breakthrough curve)

Table 4. Dynamic equilibrium adsorption capacity of AC-Br materials (30°C, inlet [Hg] 32.267 mg/m^3, flow rate 1.0 L/min.cm^3)

AC-Br materials	Dynamic equilibrium adsorption capacity (mg/g)
AC-Br-1	97.684
AC-Br-3	115.324
AC-Br-5	132.523
AC-Br-7	131.214
AC-Br-9	126.347
AC-Br-12	113.618

capacity of AC-Br-5 is highest. The reason of this phenomenon can be increase of Br/AC ratio is synonymous with increase of chemical adsorption mechanism but decrease of specific area and increase of specific weight of AC-Br materials. So the materials with Br/AC ratio of 3%-5% are optimum for Hg vapor treatment and also for economic aspect.

3.4. AC-Br material regeneration and Hg recovery

3.4.1. Batch desorption of Hg

At normal temperature and pressure, adsorbed Hg was washed by solution of 0.1N $KMnO_4$ dissolved in 1.0M HNO_3 and in other conditions as described in section 2.4. The results are presented in Fig. 7.

Based on data in Fig. 7 we can see that, after 10 fractions, almost Hg was washed out. Total Hg amount recovered from 1.0 g used material is 3.8890 mg and Hg concentration remained in AC-Br after desorption was analyzed and obtained value of 0.0426 mg/g. This means adsorbed Hg on AC-Br can be removed up to 98.9% and Hg amount remained in material was negligible.

3.4.2. Continual desorption of Hg

3 g of used material was poured in water and sucked out the air from AC pores then filled in a column by wet way. The adsorbed Hg was washed by the same

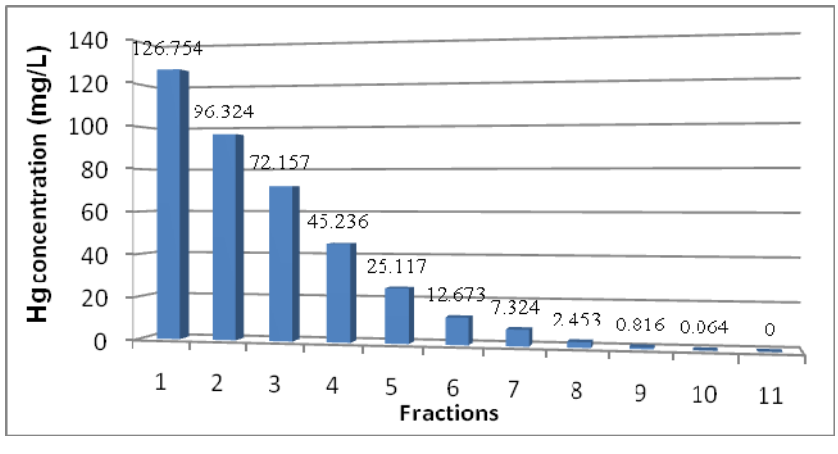

Figure 7. The Hg concentration distribution in washing fractions

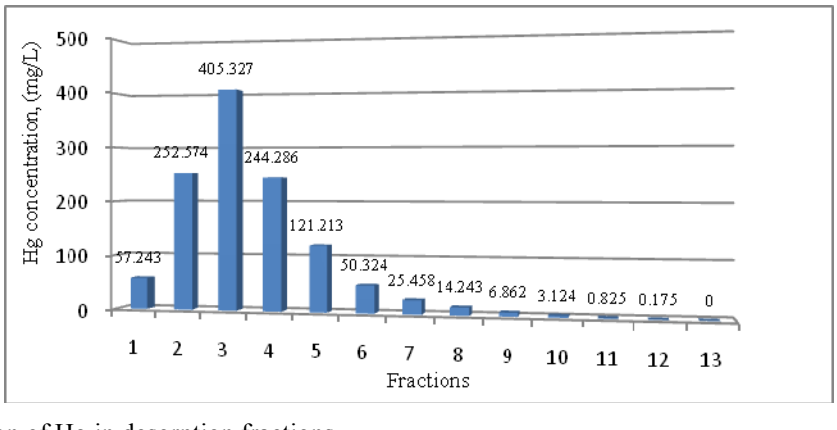

Figure 8. Concentration of Hg in desorption fractions

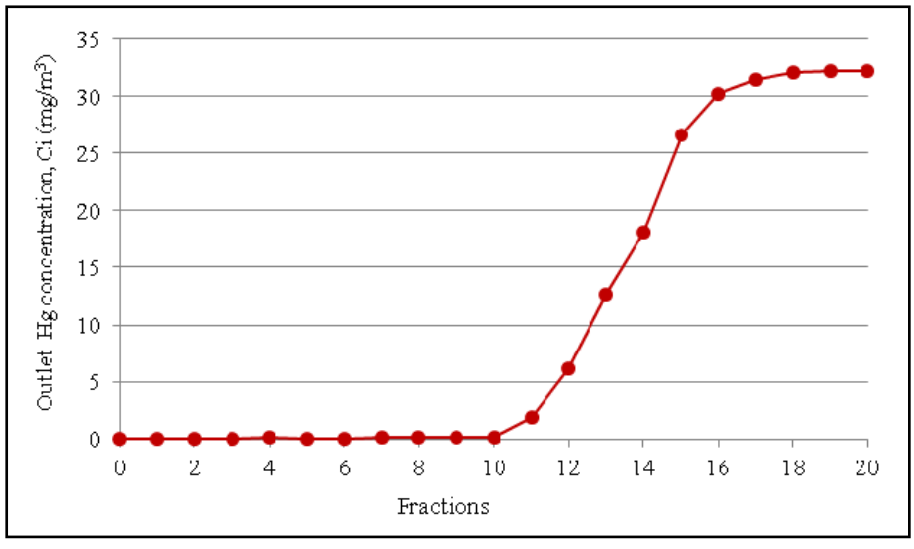

Figure 9. Dynamic adsorption curve of Hg vapor on regenerated AC-Br material

solution as used in the case of batch washing desorption. Flow rate of mobile phase in the column was 0.5 ml/min.cm^2 and the volume of every fraction was 10 ml. The Hg concentration in the fractions was analyzed by AAS with cool Hg vapor generator and the result is presented in Fig. 8.

According to data in Fig. 8, there is clear that, after 12 fractions, almost Hg in used material was washed. Total Hg amount recovered was 11.8165 mg. Hg concentration remained in washed material was analyzed and obtained value of 0.0618 mg/g and desorption efficiency reached 98.46%. The loss of the material after regeneration was determined and it was 14.68% including 8.45% of powder fraction with the size lower than 0.5 mm.

3.4.3. Hg metal recovery

Hg in 4,000 ml washed solution from continual desorption of 100 g used material was carried out for Hg metal recovery investigation. Firstly the exceed $KMnO_4$ and HNO_3 in washed solution was reduced by sodium hydrosulfite, then H_2SO_4 was added to have concentration about 0.25M. In intensively stirring, about 10 g zinc powder was slowly poured in the solution. Metal mercury or mercury amalgam was settled to the bottom. Decant the solution above precipitate. Mercury product was washed by acid solution and then by water. From 100 g used AC-Br material, the average amount of Hg metal recovered from 3 parallel examinations was 0.3954 g. The Hg recovery efficiency obtained 86.92% and about 13.08% lost according to theoretical calculation based on analytical results; but Hg in waste water was not detected.

3.4.4. Adsorption examination of regenerated material

The examination was carried out as the same those for initial material. The result was presented in Fig. 9.

In comparison with initial material, the Hg vapor appeared in effluent stream early in fraction 11th and in fraction 18th, the outlet Hg concentration was almost equal inlet concentration. The dynamic equilibrium adsorption capacity was 100.936 mg/g. It is about 13.50% lower than adsorption capacity of initial material. With this result, we can say the regenerated AC-Br material is still a good enough for Hg vapor treatment application.

4. Conclusion

The domestic coconut shell activated carbon of TraBaccompany in Northern Vietnam is suitable material for bromination. The brominated TraBac activated carbon (AC-Br) is a excellent adsorbent for mercury vapor removal. The Hg vapor capture possibility of AC-Br reached more than 99% and dynamic adsorption equilibrium capacity obtained more than 110 mg/g with Br/AC ratio in bromination upper 3%. The used material was easy to regenerate by oxidative solution of $KMnO_4$ dissolved in HNO_3. The first regenerated material was a good adsorbent for Hg vapor treatment with dynamic adsorption equilibrium capacity of more than 100 mg/g (at 30^{o}C, inlet [Hg] about 32 mg/m^3, gas flow rate 1.0 L/min. cm^2 and normal pressure). Mercury metal recovery obtained 86.92%. The TraBac AC-Br material is a excellent material for Hg vapor treatment of stack gases.

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