

Notes

Arsenic removal from water using activated carbon obtained from chemical activation of jute stick

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Arsenic removal from water in the form of As(III) and As(IV) was investigated using activated carbon obtained from jute stick using H_3PO_4 . Arsenic contaminated water was treated in two ways: (1) batch feeding system and (2) continuous flow system through a column filter. Removal of arsenic in continuous system was much better than that of batch feeding system. In the continuous system, where 0.15 ppm arsenic contaminated water was passed through a column packed with activated carbon, the maximum separation of As(III) was as high as 80%. In case of As(V) contaminated solution, almost complete separation of arsenic was achieved with activated carbon column filter. As(III) was converted to As(V) in the solution using very small amount of $KMnO_4$.

Keywords: Activated carbon, Adsorbent, Arsenic contamination, Water pollution

Arsenic contamination of underground water has created a big public health problem in many countries. The arsenic concentration of 0.05 mg/L in drinking water has been set by World Health Organization (WHO) as the upper permissible limit for Bangladesh. The higher concentrations of arsenic than the upper permissible limit can cause its deposition in human body and lead to serious human health problems. It takes about 8-14 years for symptoms to appear depending on the person¹. Therefore, the arsenic level in drinking water must be lowered than that of WHO recommended level. It is only possible by removing arsenic from water. Different attempts have been made to remove arsenic from water. They are: coagulation/precipitation^{2,3}, sedimentation, filtration⁴, adsorption⁵, magnetic separation⁶, ion exchange⁷, membrane/reverse osmosis⁸ etc.

Metal ion removal from water by activated carbon

is based on adsorption process on the solid liquid interface^{9,10}. High surface area of activated carbon with optimum micropore size is thus required for efficient adsorption of arsenic species from water. In addition, the ease of the production and yield of the activated carbon also play important roles for economic separation of arsenic from water. These lead to optimise the production conditions and characterization of activated carbon.

To meet the requirement for effective separation of arsenic from water, the aim of the present work is to develop suitable adsorbent from agricultural residues such as jute stick, which is available in many countries such as India, Bangladesh etc. In this work the high surface area activated carbon was targeted to be used as an arsenic removing material from drinking water. The jute stick was considered as raw material for high surface area activated carbon production. The activated carbon was produced by chemical activation process using H_3PO_4 as an activating agent. Before using the activated carbon for arsenic separation from water, it was characterized by measuring the specific surface area, iodine number and methylene blue number.

Experimental Procedure

After collection of jute stick, it was dried to less than 10% moisture content and cut into pieces to about 0.5 cm in size. In the previous work the jute stick was characterized by evaluating the proximate and ultimate analyses¹¹. According to the proximate analysis, the volatile fraction, fixed carbon and ash yield of jute stick were found to be 76–78, 21.4–23.4, and 0.62 wt%, respectively. From the ultimate analysis, the elemental composition of jute stick has been found to be: C, 49.79; H, 6.02; O, 41.37; N, 0.19; Cl, 0.05 and S, 0.05 wt%. Phosphoric acid (E-Merk, India, 99%) was used as an activating agent. Iodine (99.5%, Loba Chemical, India), potassium iodide (99.9%, Loba Chemicals, India), sodium thiosulphate (99.9%, Loba Chemicals, India), potassium dichromate (99.5, Loba Chemicals, India), activated carbon (Laboratory Reagent, Thomas Baker Chemicals Ltd.), and methylene blue dye (99.9%, Aldrich) were also used in the investigation.

Local made but highly precised temperature controlled stainless steel reactor was used for activated carbon production. Oven (Gallenkamp Regd, Model OV-445), Muffle furnace (Type MV2 220V 2-6kW CV3612/1973), spectrophotometer (Ogawa Seiki, Model-ANA-75), Brunauer-Emmett-Teller (BET) instrument (Model-Gemini Micrometrics 2360) and atomic absorption spectrophotometer (Shimadzu, AA-6200) were also used.

Preparation of activated carbon

Required amount of dry jute stick was mixed with 60% phosphoric acid in 1:1 ratio and kept for 12 h. Then the material was transferred into a carbonization reactor made of stainless steel with the height of 25 cm and the internal diameter of 5 cm. The temperatures of the inside and out side of the reactor were controlled by means of a temperature controller through thermocouples. The reactor was set horizontally. The nitrogen gas was passed through the reactor at the rate of 200 mL/min. The reactor temperature was kept at 200°C for 15 min and then the temperature was increased to different activation temperatures ranging from 400 to 700°C to optimize the activation temperature. After completing the activation, the products were washed with hot distilled water repeatedly in order to remove H₃PO₄ until the pH of solution reached at 6.5 and finally washed with 1% NaOH solution to completely neutralize the sample. Residual NaOH was washed out with further washing with distilled water. Then the samples were dried at 110°C for 24 h and stored in desiccators. The BET surface area of activated carbon was determined by nitrogen adsorption method at -196°C by a Gemini Micrometrics-2360. Iodine number of activated carbon was determined at 25°C based on the Standard Test Method (ASTM D4607-86)¹².

Two methods are applied for removal of arsenic from water samples. They were as follows:

(a) Batch method: About 0.1 g of activated carbon was introduced in a conical flask containing 20 mL of standard As(III) solution. The solution was stirred with magnetic stirrer for about 30 min. Then the concentration of arsenic was determined by AAS.

(b) Continuous method: About 0.5 to 1.5 g of activated carbon was loaded in a 1 cm diameter glass column. The standard As(III) solution was percolated from the top of the column and the treated water was collected from the bottom of the column in a conical flask. The arsenic concentration was measured by AAS.

The separation of As(V) was performed by the following steps: 150 mL of standard As(III) solution was taken in a 500 mL beaker. About 10 mg of KMnO₄ was added into the solution and the mixture was stirred with a glass rod for 10 min. Then this mixture was allowed to rest for 5 min. After that the solution was passed through a glass column filter as described above.

Results and Discussion

During the activation period at temperature 475°C, H₃PO₄ reacted with oxygen, hydrogen and other elements in the functional groups present in the jute stick, so as to produce volatile compounds such as H₂O, NO_x, SO_x and some of CO and CO₂. These gaseous compounds released the solid mass leaving behind the porous structure of activated carbon. The activated carbon was produced at different temperatures in view to optimize the process. The mass decreased during activation was called activation burn-off and this varied with varying activation temperatures. The yields and properties of activated carbons at different temperatures are summarized in Table 1. The steam produced in the activation process subsequently takes part in the reforming reaction of char; forming carbon monoxide and hydrogen¹³.

The yield of activated carbon decreased with increasing temperature due to the increase of activation burn-off. This was because the elevated temperature facilitated the activation burn-off and

Table 1— Effect of temperature on the yield and properties of activated carbon

Activation temperature (°C)	Yield of activated carbon (wt%)	BET surface area (m ² /g)	Iodine number (mg/g)
400	67.0	1790	1115
450	61.0	1875	1175
475	51.0	1910	1205
500	52.0	1795	1095
550	51.0	1470	887
600	50.0	1209	692
700	49.0	959	601

thus, the total mass of activated carbon decreased. On the other hand, the BET surface area and iodine number of the activated carbon derived from jute stick initially increased with increasing temperature until 475°C. Higher activation temperatures than 475°C caused the decrease of BET surface area as well as iodine number. The maximum BET surface area and iodine number were found to be 1910 m²/g and 1205 mg/g, respectively. Lower activation temperature than 475°C resulted in incomplete activation burn-off, which is attributed to the high yield but low surface area as well as iodine number of activated carbon. The higher activation temperature than 475°C also resulted in lower surface area and iodine number. High temperature activation may cause high pore volume due to the high activation burn-off; however, it may cause the destructive effect to pores, resulting in decrease of surface area and iodine number. The methylene blue dye adsorption from solution of different equilibrium concentrations on activated carbon was also studied. The results are recorded in Table 2. The amount of dye adsorption increased with increasing equilibrium concentration. The equilibrium adsorption was attained when equilibrium concentration was 8.2×10^{-4} mol/L. At the equilibrium, the dye adsorption was 399 mg/g. This amount was much higher than reported results¹⁴.

Of the two predominant forms of arsenic in water, arsenate As(V) and arsenite As(III), most treatment processes are effective for removing arsenate, but not arsenite, since arsenite is typically non-charged¹⁵ below pH 9.2. Figure 1 shows the effect of concentration on the arsenate separation capacity in batch feeding system. Although the amount of arsenic removal decreased with decreasing the concentration of As(III) due to the decrease of total amount of As(III) in the solution, the percentage separation

increased with decreasing concentration as clearly seen in Fig. 1. In this experiment the maximum removal was about 60% when 0.06 ppm standard solution was used.

The effects of concentration and the amount of adsorbent on the percentage separation in continuous flow system are shown in Fig. 2. The arsenic separation capacity increased with decreasing the solution concentration as well as with increasing the amount of adsorbent. It can be seen that in the continuous column filtration system about 80% of As(III) species can be separated from water when 1.0 g of activated carbon and 0.08 ppm arsenic solution with the flow rate of 15 mL/min were used. The concentration of As(III) in the filtrated water was as low as 0.001 ppm. This value was much lower than

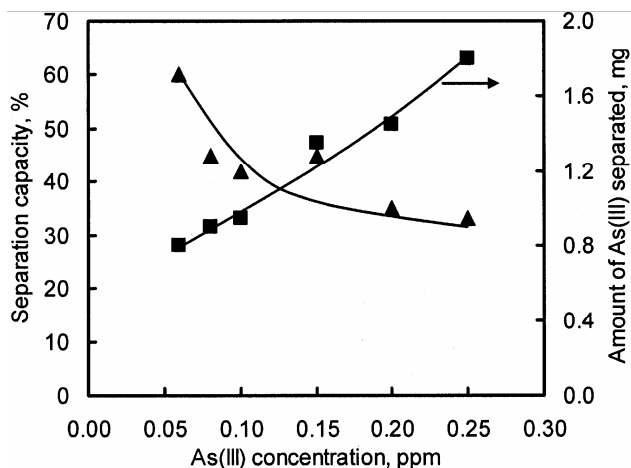


Fig. 1— Effect of As(III) concentration on separation capacity in batch feeding system at 30°C.

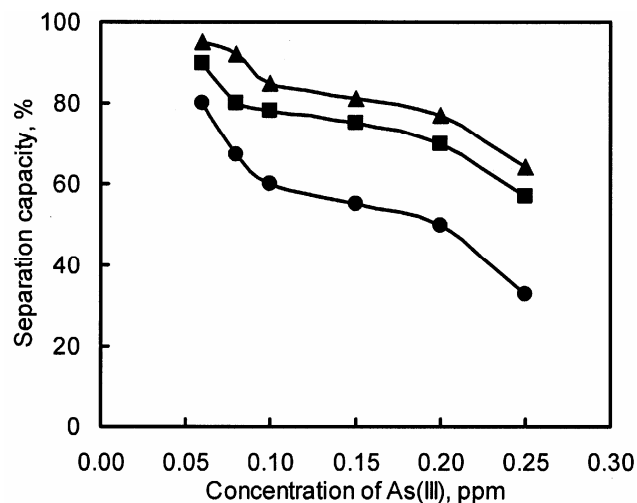


Fig. 2— Effect of As(III) concentration on separation capacity in flow system at 30°C. Amount of activated carbon ●, 0.5g; ■, 1g; and ▲, 1.5g

Table 2— Methylene blue dye adsorption on activated carbon from various concentrations at 30°C

Amount of activated carbon (m, mg)	Equilibrium concentration (10 ⁻⁵ mol/L)	Amount of dye adsorbed (x, mg)	x/m × 10 ⁻³
0.10	1.1	9.8	97.9
0.11	3.2	19.6	184.7
0.10	13.7	28.3	282.4
0.10	78.2	30.5	301.3
0.10	82.1	39.9	399.0
0.12	162.3	42.9	370.0
0.10	273.0	36.6	366.0
0.11	342.0	41.4	382.0
0.11	437.0	43.2	379.0
0.10	508.6	37.9	379.0

Table 3— Effect of As(V) concentration generated from As(III) by treating with KMnO_4 on removal capacity of activated carbon

Concentration of arsenic (ppm)	Flow rate (mL/min)	Arsenic concentration in filtrate (ppm)	Percentage separation (%)
0.40	40	0.027	93.5
0.30	40	0.007	97.7
0.2	40	0.000	100.0
0.15	40	0.000	100.0
0.10	40	0.000	100.0

that of WHO recommended upper permissible limit. The recommended limit of 0.05 ppm was also achieved even when 0.1 ppm solution, which is the usual arsenic concentration in tube well drinking water, was used. The difference between the separation using 1.5 g and 1 g of activated carbon with the same flow rate was very close and thus, further increase of the amount of adsorbent was not necessary.

The separation of arsenic as As(V) was also performed in the same column filter and the results are presented in Table 3. Before filtration the arsenic solution was treated with KMnO_4 in order to convert As(III) to As(V). When As(V) solution was passed through the column almost all of the arsenic in the solution was removed. No residual arsenic in the treated water was found either by AAS or by visible spectrophotometer method even when 0.25 ppm solution was used. The pink colour of KMnO_4 completely disappeared. The As(III) species is neutral in charge, thus the adsorption of this species on activated carbon is not chemisorption but a physical adsorption. However, the As(V) is a charged species and thus, it was adsorbed effectively on the activated carbon.

Conclusion

High surface area activated carbon is produced from jute stick using H_3PO_4 as activating agent. This activated carbon is used for arsenic separation from

water. In the continuous column filtration system, the activated carbon produced from jute stick is highly efficient to separate both As(III) and As(V) species from water. About 80% of As(III) and 100% of As(V) are removed from 0.15 ppm arsenic solution. This is also dependent on the amount of activated carbon used. More than 85% As(III) is removed from the contaminated solution when 1.5 g of activated carbon is used in the column. The complete removal of arsenic is achieved (100% separation) when the solution is pretreated with KMnO_4 even when very high concentration of arsenic solution (0.4 ppm) is used. This is due to the fact that upon oxidation the As(III) is converted to the As(V) which is highly polar species and can easily be adsorbed on the surface of the activated carbon.

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