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Removal of Atrazine from Water by Low Cost Adsorbents Derived from Agricultural and Industrial Wastes

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Abstract In the present study six adsorbents viz. wood charcoal, fly ash, coconut charcoal, saw dust, coconut fiber and baggasse charcoal were studied for their capacity to remove atrazine from water. The removal efficiency of different adsorbents varied from 76.5% to 97.7% at 0.05 ppm concentration and 78.5% to 95.5% at 0.1 ppm concentration of atrazine solution, which was less than removal efficiency of activated charcoal reported as 98% for atrazine (Adams and Watson, J Environ Eng ASCE 39:327–330, 1996). Wood charcoal was a cheap (Rs 15 kg^{-1}) and easily available material in house holds. Since wood charcoal was granular in nature, it could be used for the removal of atrazine from water to the extent of 95.5%–97.7%. Fly ash is a waste product of thermal plant containing 40%–50% silica, 20%–35% alumina, 12%–30% carbon and unburnt minerals having a high pH of 9–10. It is very cheap and abundant material and has comparatively good adsorption capacity. It was found that fly ash effectively removed about 84.1%–88.5% atrazine from water at 0.05 and 0.1 ppm levels. Coconut shell is also waste product. Therefore, both are inexpensive. The removal efficiency of atrazine from water was 92.4%–95.2% by coconut shell charcoal and 85.9%–86.3% by coconut fiber. Sawdust is generally used as domestic fuel and found everywhere. It is also very cheap (Re. 1 kg^{-1}). Baggasse charcoal is a waste product of sugar mill and abundant material. Its cost is due to transport expense, which depends upon distance from the sugar mill. The removal efficiency of sawdust and baggasse charcoal was found 78.5–80.5 and 76.5–84.6, respectively. The efficacy of chemically treated adsorbents for the removal of atrazine from water is in the order: wood charcoal > coconut shell charcoal > fly ash > coconut fiber charcoal > baggasse charcoal > sawdust.

Keywords Atrazine removal · Water · Low cost adsorbents

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), a chlorinated triazine herbicide is one of the most widely used pesticides in crops like maize, sugarcane, citrus fruits, sorghum, pineapple (Graymore et al. 2001) and has been sold under different commercial name like Aatrex, Aatratol, Bicep, and Gasaprim. Due to its extensive use, long life, high geochemical mobility (Moorman et al. 2001) and various toxic properties, (LD_{50} 1,869–3,080) it has environmental significance (Ghosh and Philip 2006; Hayes et al. 2002; Wicklund and Dich 1994) and need remediation. There are several technologies available for the removal of atrazine from water, wastewater and contaminated soil. The most commonly used being chemical treatment, incineration, adsorption, phytoremediation and biodegradation (Ghosh and Philip 2006; Chang et al. 2005; Zhu et al. 2005; Clausen and Faricius 2001). Adsorption process is a surface phenomenon, which depends upon the number of sites available, porosity and specific surface area of adsorbent as well as various types of interactions. Activated carbon due to its high surface area and porosity is very efficient in removing varieties of pesticides from water and wastewater (Sudhakar 1999; Adams and Watson 1996; Jiang et al. 2006). The activated carbon is costly, which forced the researchers to search out for low cost adsorbents for remediation (Keerthinarayana 1994; Ghosh

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and Philip 2005; Sharma et al. 2006). In the present study six adsorbents viz. wood charcoal, fly ash, coconut charcoal, saw dust, coconut fiber and baggasse charcoal were studied for their capacity to remove atrazine from water.

Materials and Methods

All the solvents were glass distilled before use. Sodium sulphate was washed repeatedly with distilled acetone and activated at 125°C for 3 h before use. An analytical grade standard of atrazine (98.2%) was used for preparation of stock solution. The pH measurements were made using Biocraft, NIG 333 pH meter. Specific surface areas of these adsorbents were measured by ethylene glycol mono ethyl ether (EGME) retention method (Carter et al. 1965) and elemental analysis was done as per standard method (Welcher 1963). Information on chemical structure was obtained by recording the spectrum of these adsorbents in potassium bromide in the range of 500–4,000 cm^{-1} using Perkin-Elmer spectrophotometer.

Wood charcoal, coconut shells and sawdust were collected from local market of Agra city. Fly ash was obtained from Kota Super Thermal Power Station, Rajasthan while baggasse charcoal was collected from Chhata sugar mill, Chhata. All adsorbent materials were washed thoroughly with distilled water to remove the presence of foreign impurities. Coconut shells were burnt and the charcoal flakes were collected before becoming ash by sprinkling water. It was again heated to red hot on a coil of an electric heater to become sufficiently porous. All adsorbents were treated with 0.1 N H_2SO_4 (1:2) and kept in the oven at 200°C for 4 h. The washed and dried materials were pulverised and sieved to get adsorbent of size 20–200 mesh. The sieved materials were washed thoroughly with distilled water to remove fine particles. The washed materials were dried at 105–110°C for 24 h and were subjected to thermal activation at 300°C for 4 h in an inert atmosphere. The activation was carried out under closely controlled conditions to obtain optimum properties. The materials thus obtained were sieved to the desired particle size 30–100 mesh. Finally, materials were stored in a vacuum desiccator until required.

Adsorbents were tried to determine their efficacy to remove atrazine from water by column elution technique. Glass columns (45 cm × 2 cm) were taken and plugged with cotton, over which 5 g of acid washed sand was kept. Adsorbent (5 g) was loaded into the column, topped with a cotton plug and was washed with 25 mL distilled water. Water sample (500 mL) was fortified with atrazine at 0.05–0.1 ppm levels and passed through the column. Flow rate was adjusted at 5 mL min^{-1}. The eluate was collected in a beaker. 10 mL fraction was taken in a 100 mL separatory funnel and mixed with 10 mL of saturated NaCl solution. It was then extracted sequentially thrice with 20 mL ethyl acetate each time, pooled and passed through a layer of anhydrous sodium sulphate. The extract was evaporated using rotary vacuum evaporator. Final residues were dissolved in n-hexane for GC analysis. In addition, blank that is atrazine in aqueous solution with out adsorbent were simultaneously processed to determine the pesticide loss during processing. No significant loss of atrazine was observed during processing. Analysis of atrazine was done by using a Thermo-Finnigan Trace 2000 model GC equipped with ^{63}Ni-ECD and BP-5 capillary column (30 m × 0.25 mm, 0.25 μm) was used. The carrier gas was high purity nitrogen (IOLAR I) with a flow rate 1 mL min^{-1}. The injector, column and detection temperature were maintained at 250, 220 and 300°C. The limit of detection and limit of quantification for atrazine was 0.001 and 0.01 ng, respectively, on the basis of S/N ratio 3:1 and 10:1.

Results and Discussion

Preliminary studies revealed that the adsorbent materials are quite stable in water, salt solutions, dilute acids, dilute bases and organic solvents. The various characteristics of activated charcoal derived from various materials are given in Table 1.

The removal of atrazine by six adsorbents from water was examined (Table 2). The removal efficiency of different adsorbents varied from 76.5% to 97.7% at 0.05 ppm concentration and 78.5% to 95.5% at 0.1 ppm concentration of atrazine solution, which was less than removal efficiency of activated charcoal reported as 98% for atrazine (Adams and Watson 1996). Wood charcoal was a cheap (Rs. 15 kg^{-1}) and easily available material in house holds. Since wood charcoal was granular in nature, it could be used for the removal of atrazine from water to the extent of 95.5%–97.7%. Fly ash is a waste product of thermal plant containing 40%–50% silica, 20%–35% alumina, 12%–30% carbon, and unburnt minerals having a high pH of 9–10. It is very cheap and abundant material and has comparatively good adsorption capacity. It was found that fly ash effectively removed about 84.1%– 88.5% atrazine from water at 0.05 and 0.1 ppm levels. Coconut shell is also waste product. Therefore, both are inexpensive. The removal efficiency of atrazine from water was 92.4%–95.2% by coconut shell charcoal and 85.9%–86.3% by coconut fiber. Sawdust is generally used as domestic fuel and found everywhere. It is also very cheap (Re. 1 kg^{-1}). Baggasse charcoal is a waste product of sugar mill and abundant material. Its cost is due to transport expense, which depends upon distance from the sugar mill. The removal efficiency of sawdust and baggasse charcoal was found 78.5–80.5 and 76.5–84.6, respectively. The efficacy of chemically treated adsorbents for the removal of atrazine from water is in the order: wood charcoal

Table 1 Physico-chemical characteristics of various adsorbents

Adsorbent	C (%)	N (%)	H (%)	Ash (%)	Specific surface area ($m^2\ g^{-1}$)
Wood charcoal	78.2	0.85	2.4	1.2	442
Coconut shell charcoal	68.7	0.38	1.95	2.5	363
Fly ash	64.2	0.21	1.23	0.98	272
Coconut fiber charcoal	58.9	0.42	2.1	4.2	312
Baggasse charcoal	52.3	0.32	1.8	3.2	228
Sawdust	42.3	0.31	1.62	3.5	202

Table 2 Efficiency of adsorbents for atrazine removal from water

Adsorbent	Concentration of atrazine ($\mu g\ L^{-1}$)		Removal (%)[a]
	Before treatment	After treatment	
Wood charcoal	50	0.2–2.4	97.7 ± 1.1
	100	2.6–6.4	95.5 ± 1.9
Coconut charcoal	50	0.8–3.6	95.2 ± 1.4
	100	1.8–12.2	92.4 ± 5.3
Fly ash	50	1.2–11.6	88.5 ± 5.3
	100	8.4–25.8	84.1 ± 8.9
Coconut fiber	50	3–10.4	86.3 ± 3.7
	100	5.2–22.2	85.9 ± 8.5
Baggasse charcoal	50	7.4–15.6	76.5 ± 4.1
	100	3.6–27.2	84.6 ± 11.8
Sawdust	50	4.4–14.4	80.5 ± 5
	100	17.2–36.3	74.7 ± 9.9

[a] Data represent the mean ± SD of three separate samples

> coconut shell charcoal > fly ash > coconut fiber charcoal > baggasse charcoal > sawdust.

Atrazine is a triazine herbicide (Fig. 1) which is both moderately soluble (38 mg L^{-1} at 22°C) and moderately hydrophobic (log $K_{ow} = 2.3–2.7$). It is not significantly protonated above its pK_a of 1.7 (approximately). Thus atrazine is significantly protonated by addition of hydrogen at the p-nitrogen position only at very low pH ($<\sim 3.7$), but may be prone to a slightly polar character in aqueous solutions. Welhouse and Bleam observed four conformational isomers of atrazine due to delocalization of lone pair electrons on the side chain nitrogens into the triazine ring, allowing restricted rotation of the side chains (Welhouse and Bleam 1992). This charge separation creates conditions favorable for hydrogen bonding interactions involving either the acidic NH protons of the alkyl amino side chains or the basic lone pair electrons on the triazine ring or both. This is more pronounced in polar solvents. The IR spectrum of the activated adsorbents showed weak and broad peaks in the range of 3,853–500 cm^{-1}. Approximate FT-IR band assignment indicated the presence of carbonyls, carboxyls, lactones, phenols, olefinic and aromatic structures. The 1,800–1,540 cm^{-1} band is associated with C=O stretching mode in carbonyls, carboxylic acids and lactones and C=C bands in olefinic and aromatic structures, whereas the 1,210–1,000 cm^{-1} band was assigned to the C–O stretching and O–H bending modes in phenols and carboxylic acids. The assignments of a specific wave number to a given functional groups overlap and shift, depending on their molecular structure and environment. Shifts in absorption positions can be caused by the factors such as intramolecular and intermolecular hydrogen bonding, steric effects and degrees of conjugation.

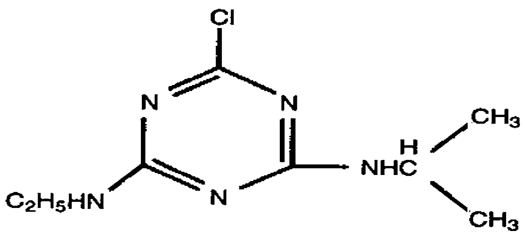

Fig. 1 Atrazine

This study reveals that adsorption of atrazine was due to large surface area and higher carbon content as well as various types of interactions between adsorbent and adsorbate. However, further study is required to gather more information on the mode of interaction. Activated charcoal has been predominantly used for removal of volatile organic compounds in drinking water as an adsorbent (Sudhakar 1999; Adams and Watson 1996; Jiang et al. 2006). The surface area of activated carbon is very large, in the order of 300–900 $m^2\ g^{-1}$ (Adams and Watson 1996) making it effective for adsorbing chemical compounds. Though the surface area of these chemically treated low cost adsorbents are less than that of activated charcoal, these are very efficient and cost-effective and hence can be used as the adsorbent for removal of atrazine from water within the maximum contamination limit which is 2 $\mu g\ L^{-1}$ for atrazine according to WHO.

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