

Performance Evaluation of Waste Activated Carbon on Atrazine Removal from Contaminated Water

Pranab Kumar Ghosh¹ and Ligy Philip²

¹Civil Engineering Department, Indian Institute of Technology, Guwahati, India

²Civil Engineering Department, Indian Institute of Technology, Madras, India

In this study, the potential of spent activated carbon from water purifier (Aqua Guard, India) for the removal of atrazine (2 chloro-4 ethylamino-6-isopropylamino-1, 3, 5 triazine) from wastewaters was evaluated. Different grades of spent activated carbon were prepared by various pretreatments. Based on kinetic and equilibrium study results, spent activated carbon with a grain size of 0.3–0.5 mm and washed with distilled water (designated as WAC) was selected for fixed column studies. Batch adsorption equilibrium data followed both Freundlich and Langmuir isotherm. Fixed bed adsorption column with spent activated carbon as adsorbent was used as a polishing unit for the removal of atrazine from the effluent of an upflow anaerobic sludge blanket (UASB) reactor treating atrazine bearing domestic wastewater. Growth of bacteria on the surface of WAC was observed during column study and bacterial activity enhanced the effectiveness of adsorbent on atrazine removal from wastewater.

Key Words: Waste activated carbon; Adsorption; Atrazine removal; Column study; Regeneration; UASB.

INTRODUCTION

Atrazine (2 chloro-4 ethylamino-6-isopropylamino-1, 3, 5 triazine) is one of the most widely used herbicides. Removal of pesticides from contaminated water by activated carbon adsorption is considered as one of the best available technologies (BAT). However, pesticides removal from wastewater containing dissolved organic carbon (DOC) by adsorption seems to suffer due to nonselective nature of the activated carbon, which adsorbs both pesticides as well as DOC. This

Address correspondence to Ligy Philip, Civil Engineering Dept., Indian Institute of Technology, Madras, India; E-mail: ligy@iitm.ac.in

leads to the early exhaustion of the adsorbent. This directed the researchers to search for low-cost adsorbent for the combined removal of atrazine as well as DOC. Clay minerals, soils, fly ash, inactive biomass, and wood charcoal are few among low-cost adsorbents which have been used as adsorbent for the removal of various pollutants from wastewater.^[1] Wood charcoal proved to be an effective low-cost adsorbent for the removal of lindane^[2] and endosulfan^[3] from the water environment. Recent studies on atrazine adsorption on iron oxides,^[4] Quartz, Calcite, Kaolinite, and α -alumina^[5] showed that only Kaolinite was suitable for the adsorption of atrazine.

In the present investigation, performance of waste activated carbon on atrazine removal from wastewater was studied.

MATERIALS AND METHODS

Materials

Chemicals

All the chemicals used in the present investigation were of analytical reagent grade (purity > 98%). Rallis India Limited, Mumbai, India, had supplied atrazine of technical grade (purity = 98%). WatersTM Sep-Pak[®] Cartridge (Sep-Pak C18 cartridge with pore size 0.45 μm) used for the extraction of atrazine was procured from Waters (Milford, MA, USA).

Adsorbent

The adsorbent selected in the present study was a waste charcoal. Eureka Forbs Limited, India, markets water purifier with the brand name of Aqua Guard in India. Nowadays, such water purifiers are commonly used in hospitals, commercial and educational institutes, and households to enhance the quality of tap water. Such a water purifier contains 200–300 g of activated carbon impregnated with 0.2% silver depending upon the size and capacity of the unit. The uniform grain size of activated carbon is around 3 mm. The useful life of activated carbon varies from 6 months to 1 year, and it is then replaced by fresh activated carbon. Wasted activated carbon from 5–6 water purifiers was collected. This was used as the raw adsorbent in the present study. Usually this exhausted activated carbon is thrown away as a solid waste.

Pretreated Adsorbents

A portion of the wasted activated carbon was pulverized and sieved through the sieves with pore sizes of 1 mm, 500 μm , and 300 μm . Two fractions of pulverized wasted activated carbon (PWAC) of grain size between 0.5 mm–1 mm and 0.3 mm–0.5 mm were considered. Wasted activated carbon (without

pulverization) and pulverized fractions of wasted activated carbon (WAC) were pretreated. For pretreatment of an adsorbent, about 20 gm of the adsorbent was taken in a 250 mL capacity glass beaker (Borosil, India) and the adsorbent slurry was stirred with magnetic stirrer at a slow speed (60–80 rpm) for 15 min to remove suspended and washable contaminants. The adsorbent was washed twice with 100 mL of distilled water with slow stirring for 5 min each, kept in oven for 4 h at a temperature of 150°C to remove any volatile materials present within the pores of the grain.^[6] After cooling, the adsorbent was kept in a dry container. To prepare acid treated adsorbent, distilled water washed wasted activated carbon was kept immersed overnight in 200 mL of 1N acid solution in a 250 mL glass beaker (Borosil, India). Sulfuric acid, hydrochloric acid, and nitric acid were employed for the acid treatment. The adsorbent was then washed with distilled water several times to get the conductivity of washed water about 4 μ S/cm and pH in between 6.8–7.2. Then it was kept in an oven at a temperature 150°C for 4 h to remove any volatile materials present within the pores of the grains.^[6] After cooling, sieved adsorbent was properly stored. Details about the type of adsorbent, sizes, and pretreatment employed in the present study are given in Table 1.

Analytical Methods

Atrazine Determination

Regular measurement of atrazine was carried out in a UV-visible spectrophotometer (model UV-160A, Shimadzu, Japan). Atrazine was extracted from wastewater by liquid-liquid separation process using dichloromethane as extractant. The detail of extraction procedure is described elsewhere.^[7] Extracted atrazine in dichloromethane was measured in UV-visible spectrophotometer keeping dichloromethane as blank. The spectra were taken at a range of 220–250 nm keeping dichloromethane as reference. Maximum absorbance was observed at 228.8 nm. Detectable limit of atrazine by this method is 0.1 mg/L.

Table 1: Details about the adsorbents used in the present study.

No.	Source	Designation	Size	Pretreatment employed
1	RWAC [#]	RWAC-1	3 mm	Distilled water
2	RWAC [#]	RWAC-2	3 mm	H ₂ SO ₄ (1 N)
3	RWAC [#]	RWAC-3	3 mm	HCl (1 N)
4	RWAC [#]	RWAC-4	3 mm	HNO ₃ (1 N)
5	PWAC [*]	PWAC-1	1–0.5 mm	Distilled water
6	PWAC [*]	PWAC-2	1–0.5 mm	HNO ₃ (1 N)
7	PWAC [*]	PWAC-3	0.5–0.3 mm	Distilled water
8	PWAC [*]	PWAC-4	0.5–0.3 mm	HNO ₃ (1 N)

[#]RAWC = Raw waste activated carbon without pulverization.

^{*}PWAC = Pulverized waste activated carbon.

Gas Chromatographic Method of Atrazine Determination

Atrazine measurement at low concentration was made in gas chromatograph (model GC-14A, Shimadzu, Japan). The procedure followed is described below.

Sample Extraction

Atrazine was extracted from 25 mL of wastewater thrice by 5 mL of ethyl acetate each time. Ethyl acetate being lighter than water (specific gravity = 0.9) remained in upper part of the separating layer. Lower part (i.e., wastewater) of the content of separating funnel was collected in a 25 mL volumetric flask without filtration, whereas the upper part (ethyl acetate containing atrazine) was allowed to pass through a filter paper topped with a bed of 2 gm of anhydrous sodium sulfate kept on glass wool. Wastewater portion was transferred again to the same separating funnel and the procedure was repeated twice using 5 mL of ethyl acetate each time. Final volume was adjusted to 10 mL using dry nitrogen gas before analysis in gas chromatograph. Extraction efficiency of atrazine by this process was $93 \pm 0.55\%$. Electron capture detector (ECD, Radioisotope Nuclide ^{63}Ni) and 1.5% OV-17 column of 3 m length and 1/8" internal diameter using pure nitrogen as carrier gas was used for atrazine determination in GC. Initial and final column temperature was 210°C , injector temperature was 225°C , and carrier gas flow was maintained at the rate of 70 mL/min. 15 μl of extracted sample was injected into injection port for atrazine determination. Detection limit of atrazine was 0.5 μg . Before each run, instruments were standardized with anticipated atrazine concentration range.

Scanning Electron Microscopy (SEM) of Adsorbent

SEM picture and EDAX analysis of adsorbent was carried out in the present investigation. Adsorbent samples collected before and after adsorption study were air-dried and then kept in vacuum desiccators before analysis. The dry sample was mounted on gold sample holder and coated with carbon in a sputter coating unit and scanned using a scanning electron microscope (model JSM-5800, JOEL Company, Japan) at an accelerating voltage of 20 kV. The elemental analysis of the adsorbent was performed using the Kevex apparatus attached to SEM (model JSM-5800, JOEL, Japan).

Experimental Methods*Kinetic Study and Screening of Adsorbent*

Polyethylene bottles (Tarson Co. Ltd., India) of 150 mL capacity were used for this experiment. A suitable adsorbent dose and 100 mL of distilled water spiked with atrazine were taken in such bottles and placed in a rotary shaker

(INSTIND, India) inside a temperature controlled chamber at an agitation speed of 145 rpm. The temperature inside the chamber was maintained at $35 \pm 0.2^\circ\text{C}$. The reaction mixture consisted of 100 mL of distilled water spiked with 5 mg/L of atrazine and an adsorbent dose of 2 g/l. The same volume of water spiked with 5.0 mg/L of atrazine without adsorbent was also run simultaneously as a control. At different time intervals up to 15 h, the samples were withdrawn from the bottles in self-scarifying mode and were filtered through Whatman No. 40 filter paper using filtration assembly. The blank was also filtered in the same manner. The filtrates were analyzed for residual atrazine concentration.

Equilibrium Study

Equilibrium study was performed using bottle point isotherm technique in a series of 150 mL polyethylene bottles at a constant temperature of $35 \pm 0.2^\circ\text{C}$ as suggested by Sontheimer, Crittenden, and Summers.^[8] 100 mL of distilled water spiked with 5 mg/L of atrazine was poured into a series of 150 mL polyethylene bottles containing varying amounts of adsorbent. The bottles were placed on the shaker immediately after being filled up with the above liquid. The contents of the bottles were agitated in the shaker for a period equal to the equilibrium time determined in the kinetic experiment. A blank with same amount of liquid without adsorbent was subjected to the same procedure to serve as the control. After the selected contact time had elapsed, the contents of the bottle were filtered through Whatman No. 40 filter paper connected to a filtration assembly.

Fixed-Bed Upflow Adsorption Column Study

The characteristics of UASB influent (atrazine spiked domestic wastewater) are given in Table 2(a), and the characteristics of the effluent from UASB reactor, which was the fixed column influent, is presented in Table 2(b). A glass column of 50 cm length and 1.5 cm internal diameter was used as packed bed adsorption column in the present study. The bed depth was kept as 20 cm. Wastewater was passed through the adsorption bed from the bottom to the top

Table 2(a): Characteristics of raw domestic wastewater (RDW).

Parameter	Value	Parameter	Value
pH	7.17 ± 0.20	P_{total} (mg/L)	6 ± 1
Alkalinity (mg CaCO_3/L)	353 ± 15	$\text{PO}_4^{3-}\text{-P}$ (mg/L)	3 ± 1
Total COD	171 ± 28	$\text{SO}_4^{2-}\text{-S}$ (mg/L)	2 ± 0.5
Soluble COD (mg/L)	142 ± 12	VFA (mg/L)	6 ± 2
Suspended solid (mg/L)	20 ± 5	Fe	Nil
VSS (mg/L)	15 ± 3	Cu	Nil
TKN (mg/L)	21 ± 4	Ni	Nil
$\text{NH}_4^+\text{-N}$	15 ± 3	Cd	Nil

Table 2(b): Characteristics of the influent wastewater to adsorption columns.

Parameter	Concentration
COD _{Soluble}	27 ± 2 mg/L
COD _{Total}	29 ± 3 mg/L
Atrazine	2,588 ± 0.13 mg/L
pH	7.1 ± 0.05
VFA	11 ± 2 mg HAc/L
Alkalinity	122 ± 5 mg CaCO ₃ /L
NH ₃ -N	17 ± 1.5 mg/L
PO ₄ ³⁻ -P	4.8 ± 1 mg/L
SO ₄ ²⁻ -S	0.05 ± 0.01 mg/L

using a peristaltic pump (model pp 20, Miclins, India) with an overflow rate of 4.95 m³/m² · h equivalent to an upflow velocity of 8.25 cm/min. Upflow mode was selected to minimize the channeling effects inside the column. The flow rate of wastewater through the column was thus kept the same as that of the feeding rate to UASB reactor (14.58 mL/min). The empty bed contact time calculated was 2.42 min. Samples were taken at regular intervals until sorption capacity exhaustion. When effluent atrazine concentration was more than 90% of influent concentration, the column was regenerated.

Desorption and Regeneration Studies

Desorption study was carried out using the exhausted adsorbent after the column study. Desorption was done in two steps. In the first step, 100 mL of distilled water was passed through the exhausted column at the same flow rate as that of the influent. In the next step 300 mL of 5% (v/v) methanol in distilled water was passed through the column at the same rate as that of earlier and the effluent concentration of atrazine was measured. Methanol is a good solvent for atrazine as well as a preferred food for microbes. The adsorbent was washed with 1N HNO₃ followed by distilled water until the pH and TDS came down to a normal value. After the regeneration, the column was reused for the treatment of UASB effluent containing atrazine.

RESULTS AND DISCUSSION

Kinetic Study

Kinetics of atrazine adsorption by various grades of waste activated carbon (Table 1) is given in Figure 1. Among the various grades of pulverized waste activated carbon (PWAC), PWAC-3 (grain size between 0.3 mm and 0.5 mm and pretreated with distilled water) and PWAC-4 (grain size between 0.3 mm to 0.5 mm and pretreated with 1 N HNO₃) showed almost the same performance. In all the cases, within the first 1.25 h rapid adsorption of atrazine was observed.

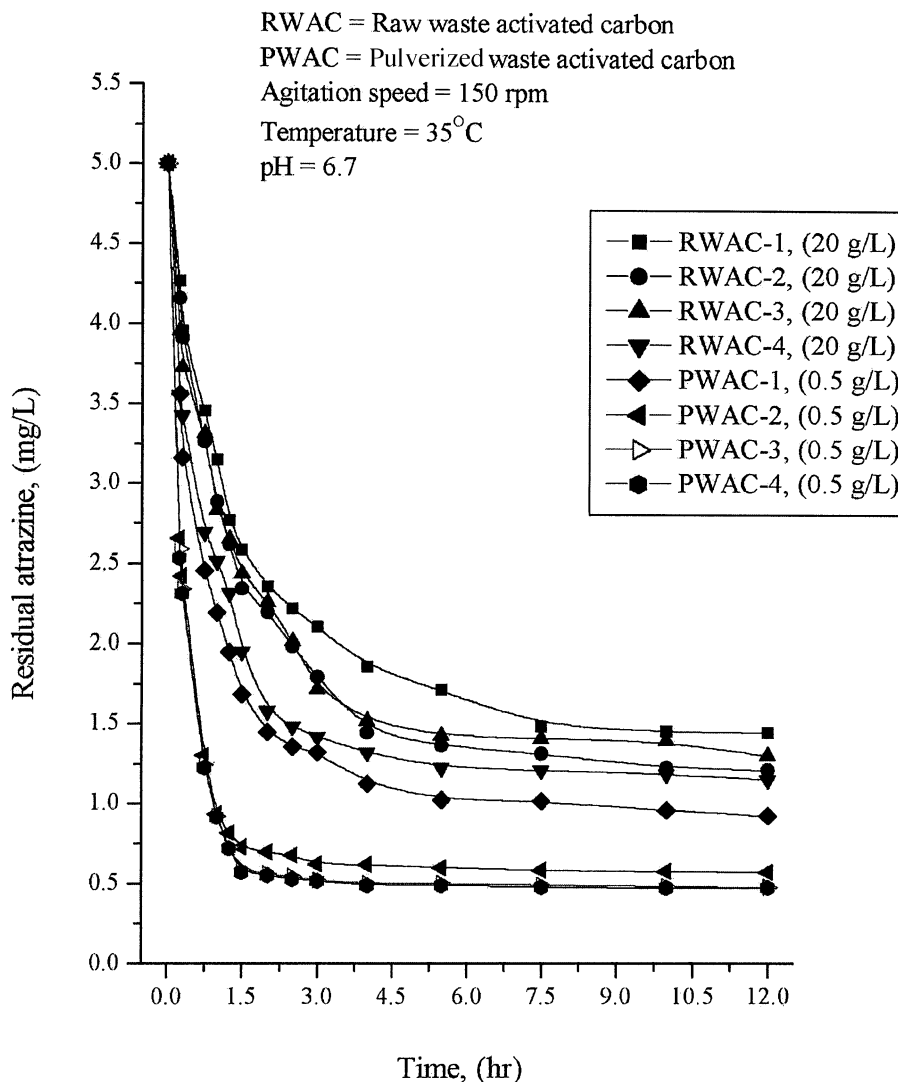


Figure 1: Kinetics of atrazine adsorption by raw and pulverized waste activated carbon.

Removal of atrazine by PWAC-3 and PWAC-4 after 1.25 h was 87.5% and 87.9%, respectively. After 2 h, atrazine removal was 88.8% and 88.9%, respectively. No significant atrazine removal was observed after 2 h. Hence, 2 h was considered as the equilibrium time for further studies.

There was no significant effect of pretreatment with mineral acid on adsorption capacity or rate. Moreover, pretreatment increases the cost of the treatment process along with other secondary waste generation, which needs to be attended. Hence, among the eight grades of adsorbents, PWAC-3 was selected for further studies, which required only distilled water washing. In subsequent

Table 3: Adsorption rate constant for different adsorbents.

Adsorbent	Rate constant (mg/g/h ^{1/2})	Contact time* (h)
WC	0.2626	2.0
RWAC-1	0.0945	2.0
RWAC-2	0.103	2.0
RWAC-3	0.1027	2.0
RWAC-4	0.1251	2.0
PWAC-1	5.6273	1.25
PWAC-2	8.5618	1.0
PWAC-3	8.6877	1.0
PWAC-4	8.7479	1.0

*Contact time up to which the kinetic data plotted for the determination of rate of adsorption show linearity.

sections, PWCA-3 is designated as waste activated carbon (WAC) unless otherwise specified.

Adsorption rates of various adsorbents are given in Table 3. The rate constants were determined by considering the linear portion of adsorption kinetics data as entire data range did not fall in a straight line. Similar trend was observed by other researchers while studying cadmium adsorption onto various low-cost adsorbents^[9] and biosorbents.^[10] Results show that the adsorption rate varied considerably with grain size of waste activated carbon employed.

Equilibrium Study

Atrazine adsorption onto WAC from atrazine spiked distilled water fit well with both Freundlich and Langmuir isotherms and is shown in Figures 2 and

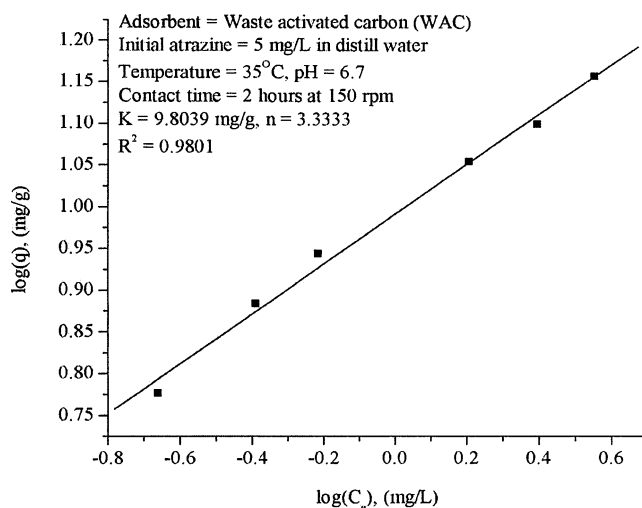


Figure 2: Linearized Freundlich isotherm for atrazine adsorption from distilled water by waste activated carbon (WAC).

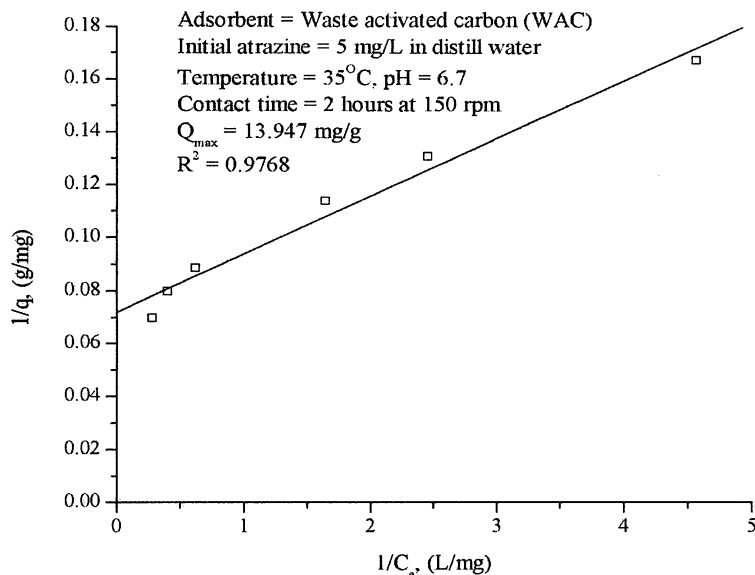


Figure 3: Linearized Langmuir isotherm for atrazine adsorption from distilled water by waste activated carbon (WAC).

3, respectively. Isotherm constants are given in Table 4. Adsorption data do not follow BET isotherm and are not presented in this report. The maximum specific adsorption capacity (Q_{max}) calculated using Langmuir isotherm for WAC for removing atrazine from distilled water was 13.947 mg/g.

Effects of Dissolved Salts and Ions on Atrazine Adsorption by WAC

Inorganic and ionizable organic salts present in the water change the ionic strength of the water and influence the adsorption process significantly. Atrazine manufacturing plant effluent and atrazine contaminated domestic wastewater contains manyfold more dissolved organic and inorganic matter than atrazine contaminated surface and subsurface water. These solutes can have negative, neutral, or positive effects on the adsorption capacity of the adsorbent.^[11–14] It was observed that calcium chloride enhanced the fulvic acid adsorption in granular activated carbon (GAC),^[13] whereas the naturally

Table 4: Adsorption isotherm constants for adsorption of atrazine by WAC.

Langmuir isotherm coefficients			Freundlich isotherm coefficients		
Q_{max}	a	R^2	n	K	R^2
13.947	3.2591	0.9768	3.3333	9.8039	0.9801

Unit: Q_{max} =mg/g.

R^2 = Regression coefficient.

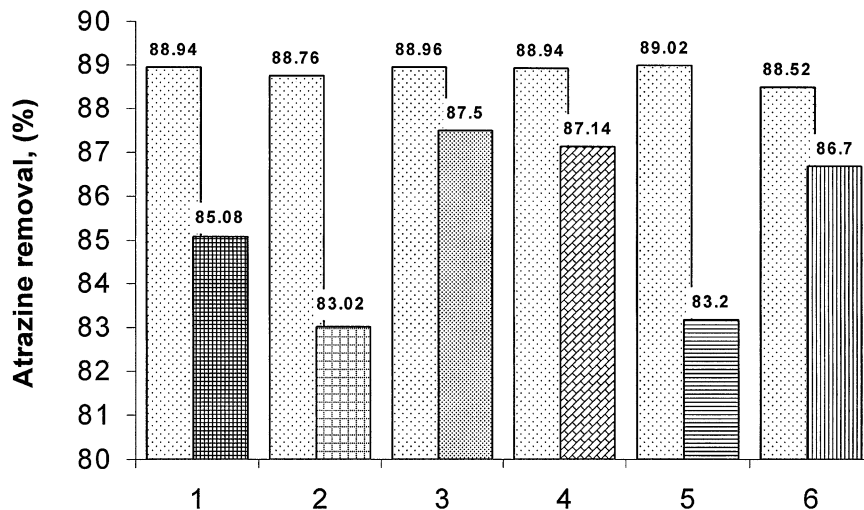


Figure 4: Effect of inorganic ions on atrazine adsorption by WAC.

occurring humic acid had no effects on the removal of polynuclear aromatic hydrocarbons (PAH).^[12] The result (Fig. 4) showed that there was almost no effect of calcium ion ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) on the adsorption capacity of WAC. Presence of dextrose at a concentration higher than 30 mg/L in the wastewater has reduced the adsorptive capacity of WAC significantly. Effects of other inorganic salts like ammonium, phosphate, and calcium on atrazine adsorptive capacity of WAC were less. These ions are very commonly present in water and wastewater systems. The competition of these ions for adsorption sites may be less compared to atrazine. Hydrophobicity is an important factor, which affects the adsorption process significantly. Atrazine is more hydrophobic than all other inorganic salts used for the present study.

Fixed-Bed Adsorption Column Study

Upflow packed bed adsorption column is used to assess the performance of WAC in removing atrazine from the effluent of upflow anaerobic sludge blanket (UASB) reactor treating domestic wastewater in continuous mode of operation. Although downflow adsorption column is easy to operate, upflow adsorption column is more suitable for wastewater containing large quantities of suspended solids. In addition, in upflow adsorption column, the contact between adsorbent and adsorbate are better compared to downflow-mode. Considering these points fixed bed upflow adsorption column was selected. Thirteen grams of WAC was added to the adsorption column to get a bed depth of 20 cm. The hydraulic loading rate employed in the adsorption column was $8.25 \text{ cm}^3/\text{min}/\text{cm}^2$ for which the empty bed contact time calculated was 3.35 min. The WAC (particle size between 0.3 mm and 0.5 mm) used in the present study had a dry density of $0.41 \text{ g}/\text{cm}^3$.

Breakthrough Curve

The breakthrough curves for both organic matter (in terms of chemical oxygen demand, COD) and atrazine are shown in Figure 5. The column could effectively remove all the atrazine from the wastewater for 26 h, which corresponded to a throughput volume of 23 L. As far as the organic matter removal is considered, the column performance was better. For 72 h, the effluent COD was below detectable level. Then it gradually increased. The COD value never

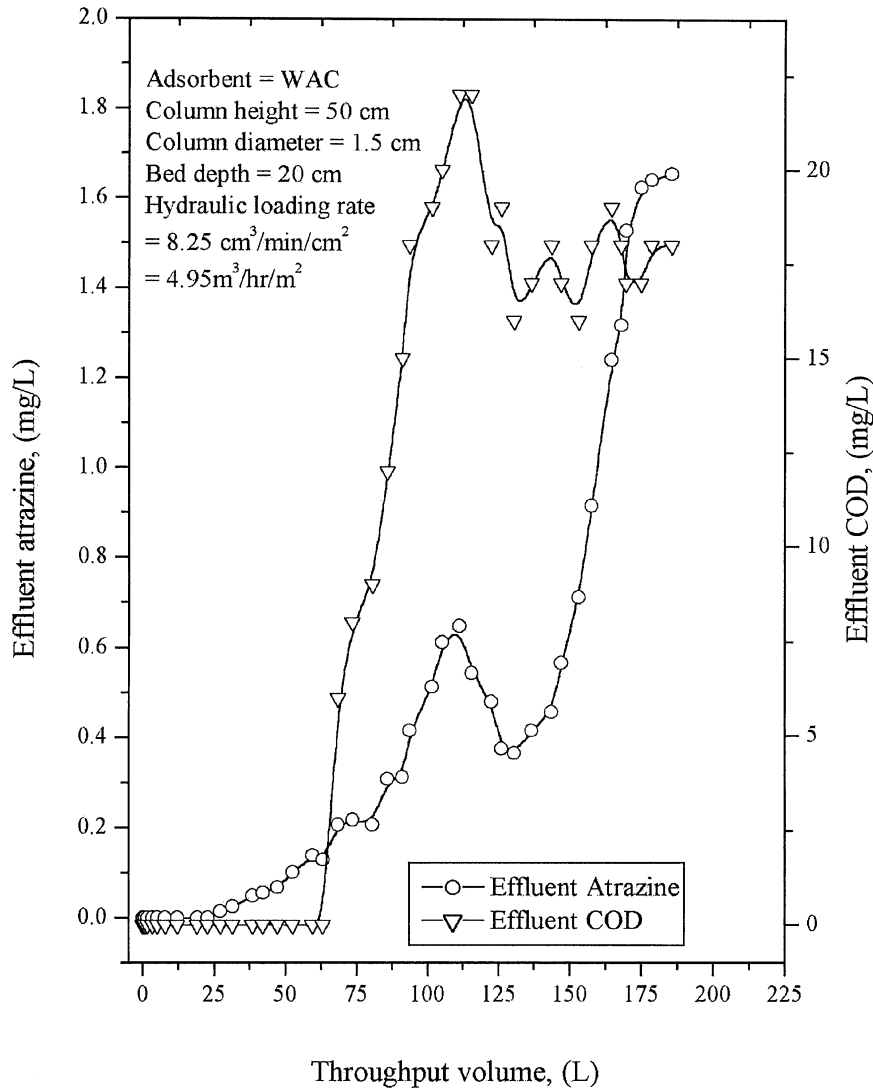


Figure 5: Breakthrough curves for waste activated carbon (WAC) removing atrazine and organic matter in fixed bed adsorption column.

exceeded 30 mg/L, which is the effluent discharge standard in terms of BOD. Here dextrose was the primary carbon source, which is highly biodegradable. Hence, COD value is almost equal to the ultimate BOD value.

The breakthrough curve for organic matter (as COD) was a steep curve, whereas in the case of atrazine it was relatively flat. This shows that the organic matter (used in the present study) is having a higher preference to WAC. This was evident from the batch studies also. As the organic matter (OM) concentration increased in the liquid phase, the percentage removal of atrazine decreased. It is reported that under the conditions prevailing in waterworks only 20–40% of the single solute capacity for trichloroethane has been achieved in a GAC fixed bed absorber at a complete breakthrough of the trace organic compound.^[15] When preloaded GAC was used for atrazine removal, the efficiency reduced to 33% compared to virgin GAC.^[14] In contrast to this, in some isotherm studies, the solid phase concentration of activated carbon for chlorinated hydrocarbons was not reduced in presence of humic substances.^[14] From these studies, it is evident that the competition for adsorption sites in GAC varies from waste to waste depending upon the constituent's chemical composition.

During the column run, until 100 h, the concentration of atrazine and organic matter (OM) had steadily increased. After this, the effluent atrazine and OM concentration started decreasing slightly though the column was operating in the same flow rate as before. This may be due to the growth of microorganisms on the adsorbent surface. They might have degraded the adsorbed OM and atrazine partially. The OM concentration in the column effluent never increased after 100 h. In case of atrazine, the effluent concentration remained almost constant for 50 more hours, and then started increasing. Initially the concentration of OM available in the adsorbent surface might not have been very high; therefore, the microorganisms must have degraded the atrazine. As the OM concentration increased, the atrazine degradation decreased. Moreover, WAC had a high affinity for OM compared to atrazine. Due to this, whatever traces of OM available might have been adsorbed by GAC, whereas atrazine came out in the column effluent.

From the column study results, the atrazine removal capacity of the WAC was calculated by considering the area under the breakthrough curve for the entire operational period until the column reached break point. In the present study, break point was considered at the time in which the effluent atrazine concentration reached almost 90% of the influent concentration. Throughout the run, 223.52 mg of atrazine was removed in the column. The specific atrazine removal capacity of WAC calculated was 17.19 mg/g, whereas the Q_{\max} value obtained from the batch studies using Langmuir isotherm was 13.947 mg/g for treating atrazine in distilled water. In fixed bed adsorption column, high concentration gradient of adsorbate is available. In batch studies, the concentration gradient, which is the driving force for adsorption, is much less. This may be one of the reasons for high atrazine adsorption capacity of WAC in the

column. Another reason must be the biological degradation. Microorganisms can grow on the surface of the adsorbent during the treatment of wastewater containing biodegradable carbonaceous material. There are several reports regarding the growth of microorganisms on the surface of the adsorbent during adsorption process.^[15–17] There can be mixed effects on the performance of adsorption column due to the growth of microorganisms. Adsorption of pollutant generally takes place mainly on the micropores (size $0.5 \mu\text{m}$) of adsorbent. As the average size of microorganisms is about $50\text{--}100 \mu\text{m}$, they cannot occupy the micropores of adsorbent and thus it affects the adsorption process.^[18] Moreover, due to metabolic activity of the microorganisms, pollutant load on the adsorbent can be reduced. On the other hand, due to excessive growth of microorganisms on the surface of the adsorbent, a layer can be formed, which can reduce the pollutant transport rate from liquid phase to adsorbent through the bio-film.^[18]

SEM Picture and EDAX Analysis

To make sure of the biological growth in the adsorption column, samples of adsorbent were taken before and after the adsorption and were analyzed using a scanning electron microscope (SEM). The SEM photographs of adsorbents before and after adsorption are given in Figures 6 and 7, respectively. From these pictures, it is clear that there was significant difference in the appearance of the adsorbent surfaces. The white clumps on the adsorbent surface represent the biomass. The EDAX analysis of the selected spots on the WAC surface was

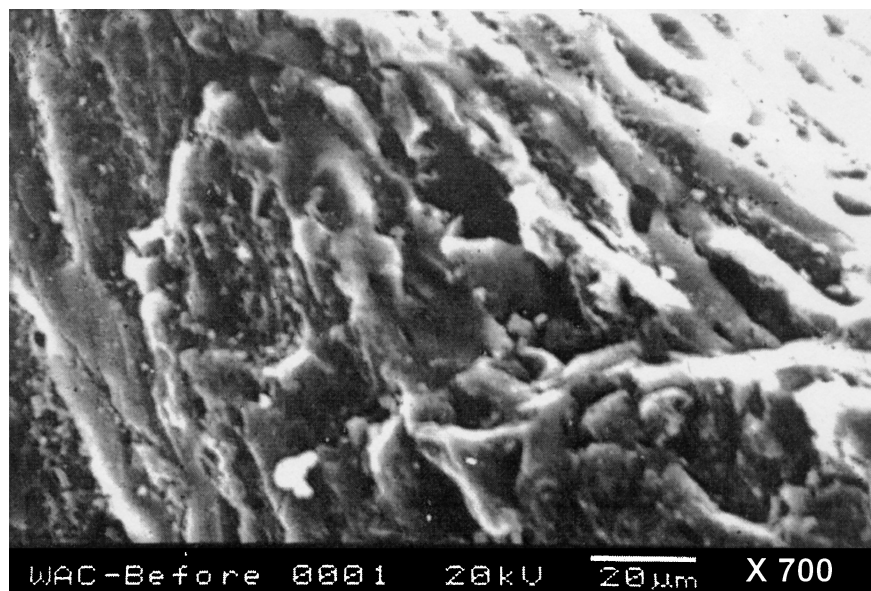


Figure 6: SEM picture of waste activated carbon before column adsorption study.

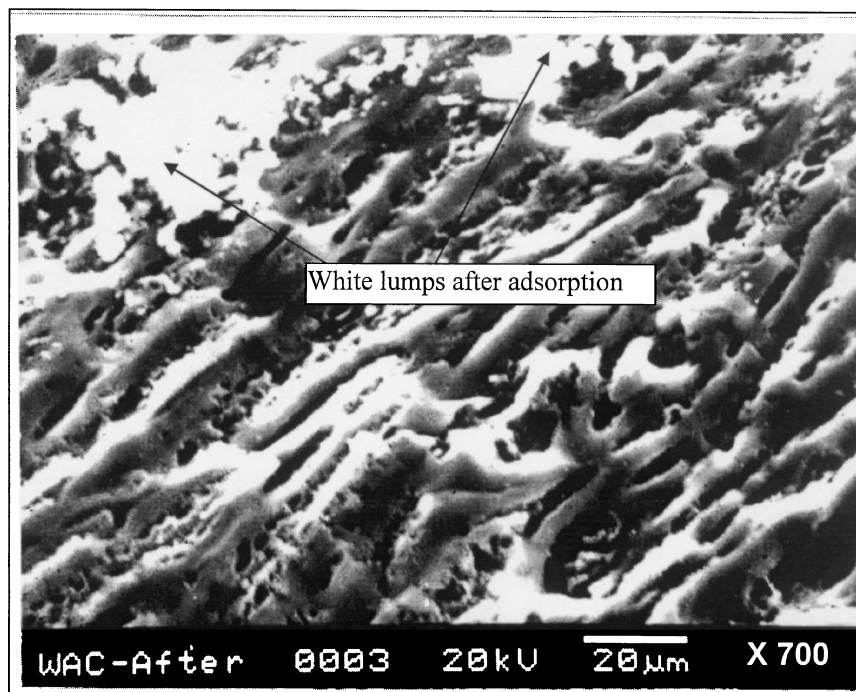


Figure 7: SEM picture of waste activated carbon after column adsorption study.

carried out. The elemental analysis of the white spot showed that it contained high concentrations of Ca, Mg, P, S, and Fe compared to the adsorbent analyzed before column study (Table 5). Even though there was some biomass growth in the column, there was no clogging or excessive pressure drop in the column. This may be due to very low concentration of OM available for the microorganisms in the column.

Table 5: EDAX analysis of adsorbent waste activated carbon (WAC).

Element	Atomic (%)	
	Before adsorption	After adsorption
Na	15.01	18.55
Al	9.07	3.32
Si	17.38	9.54
S	29.15	32.15
Ca	12.37	15.28
Fe	12.80	15.45
Mg	0.084	1.43
Ag	3.11	1.55
Cl	0.06	0.31
P	1.02	2.42
Total	100	100

Regeneration and Reuse of WAC

Economic viability of an adsorption system depends upon the regeneration potential of the adsorbent. To know the regeneration potential of WAC, the desorption study of the exhausted WAC was carried out. Five percent methanol in distilled water (v/v) was used as the eluents. Three hundred mL of the above mixture of solvents was passed through the exhausted column at a flow rate of 8.25 mL/min/cm² and then washed three times with 200 mL of distilled water in each wash. The eluent was collected and analyzed for atrazine concentration. The concentration of atrazine in methanol was 641 mg/L, which corresponds to 86.3% of the total herbicide adsorbed on the column. The OM concentration in the eluent was not measured as the methanol was contributing so much of COD. Five percent methanol in water could desorb more than 86% of the total adsorbed atrazine. The remaining 14% that was not desorbed may be due to the poor solubility of atrazine in methanol or due to the improper contact. It may be also due to the irreversible adsorption of atrazine on some adsorption sites. To see the efficiency of the regenerated WAC, it was reused for the atrazine removal. The results are presented in Figure 8 (second cycle of operation). The breakthrough curve followed almost the same trend as that of the fresh adsorbent. Up to a period of 14 h, effluent atrazine concentration was below the detectable limit. In this case also, atrazine concentration was found to be decreasing after a period of 116 h of operation. This may be due to the reduction of atrazine by the microorganisms grown on the surface of the adsorbent. The specific atrazine removal capacity of WAC in the second cycle of operation calculated was 13.26 mg/g, which is about 77% to that of the first cycle.

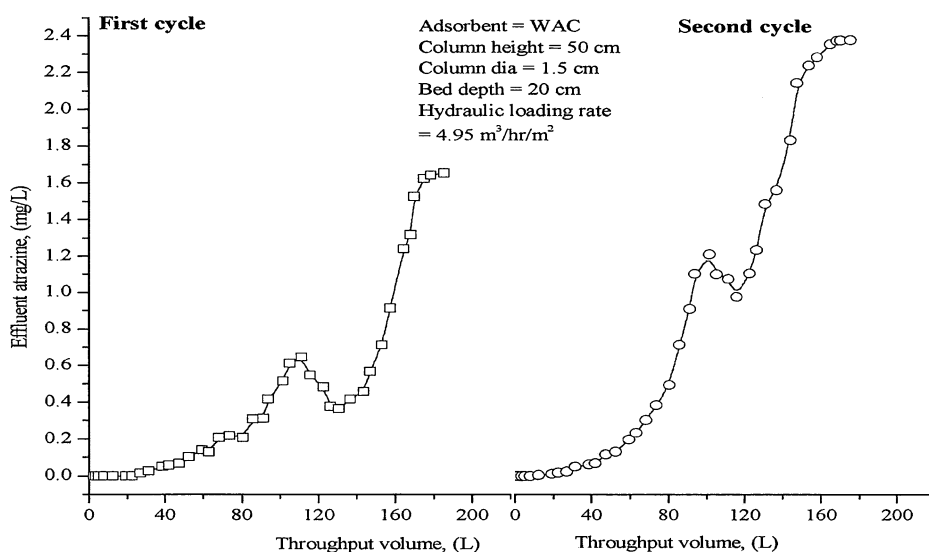


Figure 8: Breakthrough curve for WAC in first and second cycles of operation.

Results of adsorption column study before and after desorption (First and Second cycles of operation) showed that the adsorbent could be reused effectively for the treatment of wastewater containing atrazine as well as COD.

CONCLUSION

Waste activated carbon can be used as an adsorbent for the removal of atrazine from contaminated water after proper pretreatment. The adsorption data fit well with both Freundlich and Langmuir isotherm. From Langmuir isotherm, maximum adsorbent capacity (Q_{\max}) of WAC on atrazine removal from distilled water was 13.947 mg/g, whereas the column study shows that specific atrazine removal capacity of WAC from UASB treated wastewater which contains about 30 mg/L of COD was 17.19 mg/g. The adsorbent WAC supports the growth of atrazine degrading bacteria on its surface and thereby enhances the atrazine removal efficiency. WAC was able to remove atrazine effectively even in the presence of other competing pollutants generally present in wastewaters. The WAC can be reused as adsorbent at least two times before its final disposal.

REFERENCES

1. Keerthinarayan, S. Sorption of lindane from water environment by wood charcoal. Ph.D. thesis, Civil Engineering Department, Indian Institute of Technology, Kharagpur, India, 1994.
2. Keerthinarayana, S.; Bandyopadhyay, M. Sorption and desorption of lindane by wood charcoal in fixed bed reactor. *J. Environ. Sci. Health* **1997**, *B32*, 701–706.
3. Sudhakar, Y.; Dikshit, A. K. Kinetics of endosulfan sorption on to wood charcoal. *J. Environ. Sci. Health* **1999**, *B34* (4), 587–615.
4. Clausen, L.; Fabricius, I. Atrazine, Isoproturon, Mecoprop, 2,4-D, and Bentazone adsorption onto iron oxides. *J. Environ. Qual.* **2001**, *30* (3), 858–869.
5. Clausen, L.; Fabricius, I.; Madsen, L. Adsorption of pesticides onto Quartz, Calcite, Kolinite, and α -Alumina. *J. Environ. Qual.* **2001**, *30* (3), 846–857.
6. Culp, R.L.; Wesner, G.M.; Culp, G.L. *Handbook of Advanced Wastewater Treatment*, 2nd Ed. Van Nostrand Reinhold: New York, 1976.
7. Ghosh, P.K.; Philip, L.; Bandyopadhyay, M. Anaerobic treatment of atrazine bearing wastewater. *J. Environ. Sci. Health* **2001**, *B36* (3), 301–316.
8. Sontheimer, H.; Crittenden, J.C.; Summers, R.S. *Activated Carbon for Water Treatment*, 2nd Ed. (in English). DVGW-Forschungsstelle, Engler-Bunte Institute: Karlsruhe, Germany, 1998.
9. Bhattacharya, A.K.; Venkobachar, C. Removal of Cadmium (II) by low cost adsorbents. *J. Environ. Eng. ASCE* **1984**, *110*, 110–127.
10. Osman, S. Biosorption of heavy metal from water environment by Macro Fungi *V. volvacea*. Ph.D. thesis, Civil Engineering Department, Indian Institute of Technology, Kharagpur, India, 1995.

11. Fritz, W. et al. In *Activated Carbon Adsorption of Organics from the Aqueous Phase*, Vol. 1; Suffet, I.H.; McGuire, M.J., Eds. (Ann Arbor Science Publishers: Ann Arbor, MI, 1980; p. 193.
12. Randtke, S.J.; Jepsen, C.P. Effects of salts on activated carbon adsorption of Fulvic acid. *J. AWWA* **1982**, *74* (2), 84–88.
13. Haist-Gulde, B.; Baldauf, G.; Brauch, H.J. Removal of organic micropollutants by activated carbon. In *Water Pollution, Quality and Treatment of Drinking Water*. Springer-Verlag: Berlin Heidelberg, 1991; 103–128.
14. Pelekani, C.; Snoeyink, V.L. A kinetic and equilibrium study of competitive adsorption between atrazine and Congo red dye on activated carbon: The importance of pore size distribution. *Carbon* **2001**, *39*, 25–37.
15. Sontheimer, H. Design criteria and process schemes for granular activated carbon (GAC) filters. *J. AWWA* **1979**, *71* (11), 618–622.
16. Schalekamp, M. The use of GAC filtration to ensure quality in drinking water from surface sources. *J. AWWA* **1979**, *71* (11), 638–647.
17. Cairo, P.R.; McElhaney, J.; Suffet, I.H. Pilot plant testing of activated carbon adsorption systems. *J. AWWA* **1979**, *71* (11), 660–673.
18. Committee report. Assessing microbial activity on granular activated carbon. *J. Am. Water Works Assoc.* **1981**, *73* (8), 447–454.