Competitive Sorption of Pesticides onto Treated Wood Charcoal and the Effect of Organic and Inorganic Parameters on Adsorption Capacity

Yedla Sudhakar, M.ASCE[1]; and Anil Kumar Dikshit[2]

Abstract: This paper presents competitive sorption of coexisting pesticides onto treated wood charcoal and describes the effect of various water quality parameters, viz., pH, ionic strength, chloride concentration, presence of calcium and magnesium, fertilizers, humic acid, polyacrylic acid, and also the effect of coexisting pesticides on the sorption of endosulfan onto treated wood charcoal. The coexisting pesticides were found to hinder the performance of wood charcoal in removing endosulfan. Competitive uptake study revealed that endosulfan occupies more sites followed by atrazine and monocrotophos. Solubility in water could be one of the major reasons for this preferential order. The presence of humic acid was found to show much more significant influence on the performance of wood charcoal than the presence of polyacrylic acid. Among fertilizers, single superphosphate was found more influential. Most of it, among the other reasons, could be due to the competition of the coexisting molecules for the available adsorption sites on wood charcoal. Other parameters have resulted in some fluctuations in performance, but the effects are not significant. Endosulfan removal efficiency faltered at higher pH values, and ionic species did not affect the sorption as endosulfan is nonionic under neutral conditions.

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Introduction

Endosulfan, the most widely used pesticide in various parts of the world, has been catching the public as well as organizational concern upon its disastrous effect on the environment (Bakore et al. 2004; Dewan et al. 2004; Halder et al. 1989; Kumari et al. 2002; Sankararamakrishnan et al. 2005; Shukla et al. 2006). Its impact on drinking water sources made this problem even more intense (Bhattacharya et al. 2003; Dewan et al. 2004; Eichelberger and Lichtenberg 1971; Greve and Wit 1971; Guerin 2001; Halder et al. 1989; Kumari et al. 2002; Ramesh and Vijayalakshmi 2002; Schulz 2004). Responding to the severity of the problem there have been many efforts to control pesticide pollution in various spheres of the environment (Aslan and Turkman 2004; Keerthinarayana and Bandyopadhyay 1993; Shivaramaiah and Kennedy 2006; Yedla and Dikshit 1999a, 2001a). The property of hydrophobity and affinity to sediments favors adsorption mechanism for the removal of endosulfan from water environment (Kumar and Philip 2006; Yedla and Dikshit 1999a, 2001a).

Contamination of water sources with pesticides has been predominantly a rural problem, and hence the removal mechanism developed should be tailored for rural applications. In their attempts to identify a suitable and low cost adsorbent for the removal of endosulfan, Yedla and Dikshit (1999a) found that wood charcoal (WC) made of local wood has considerable adsorption capacity. After capacity enhancement efforts by means of acid treatment (1-N HNO_3) WC was found to remove 95% endosulfan from the sample of 1-mg/L initial concentration (Yedla and Dikshit 2002). Film diffusion was found to be the rate limiting process (Yedla and Dikshit 1999b). Further it was reported that the adsorption process is endothermic in nature and it is guided by physic sorption (Yedla and Dikshit 2001a).

For an adsorbent to be successful it should show promise both technically by means of superior adsorptive capacity and economically by means of higher regeneration cycles and easy sludge management. Treated WC was reported to perform well in removing endosulfan from the water environment. Its adsorptive capacity was reported to be better than that of activated WC, and the regeneration with the help of dilute methanol solution remained more than 80% even after 4 cycles of adsorption desorption (Yedla and Dikshit 2008). Authors have reported that using aerobic mixed bacterial culture could be the best way to manage the spent eluent from the adsorption process (Yedla and Dikshit 2001b,c).

Unlike the laboratory conditions, natural waters contain more than one pollutant and these pollutants, while trying for the removal of target pollutant, are known to compete for the available adsorption space resulting in change in removal efficiency for the target pollutant (Keerthinarayana and Bandyopadhyay 1993). Therefore, it is necessary to study the performance of the treated WC in removing endosulfan from water environment in the presence of the other competing pollutants. In an effort to break the final barrier for the use of treated WC to remove endosulfan under practical conditions, the authors have made an effort to study the

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[1] Professor, Department of Civil Engineering, National Institute of Technology (NIT), Warangal 506004, India (corresponding author). E-mail: s_yedla@yahoo.com

[2] Professor, Center for Environmental Science and Engineering, Indian Institute of Technology, Powai, Mumbai 400078, India.

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competitive uptake of various coexisting pesticides and also elucidate the effect of various water quality parameters on the removal efficiency of WC for endosulfan.

Materials and Methods

All the reagents used in this study were of analytical grade. *n*-hexane of 99.9% purity was used for gas chromatography (GC). Technical grade endosulfan of 98.7% purity and laboratory grade Monocrotophos were obtained from Vijayalakshmi Insecticides and Pesticides Limited A.P., India and laboratory grade Atrazine from Hindustan Lever Limited, Bombay, India. Humic acid and polyacrylic acid were procured from Aldrich Chemical Co., St. Louis.

All glassware used was of Borosil. Before every experiment, all glassware was cleaned with dilute nitric acid and repeatedly with distilled water, followed by drying at 110°C for 5 h. The glassware that came in contact with endosulfan was equilibrated with endosulfan by immersing it in an endosulfan spiked solute system of respective concentration for 10 h and washed with distilled water. A similar procedure was adopted for Tarson polyethylene bottles, which were used for batch experiments.

Analytical Methods

Standard methods were adapted for the analysis of various water quality parameters (APHA-AWWA-WPCF 1989). Gas chromatograph (GC-14A, Shimadzu, Japan) with an electron capture detector (^{63}Ni) with a 5% OV-17 stainless steel poropak column was used for endosulfan measurement. The column was of 3-m length and 3.18-mm (1/8-in.) diameter. The temperatures for column, injector, and detector were maintained at 220, 230, and 300°C, respectively. Nitrogen (99.9% purity) was used as a carrier gas at a flow rate of 50–60 ml/min. A calibration curve was made between known concentration of endosulfan and the corresponding peak areas. This curve, fitted by the method of least squares, was used to quantify endosulfan in the samples of unknown concentration. A calibration curve for a concentration range 0–5 mg/L was made for accurate measurement of endosulfan.

Synthetic Sample Preparation

Stock solution of endosulfan was prepared by dissolving technical grade endosulfan in acetone, which is water miscible and exhibits more solubility for endosulfan. A high precision balance with an accuracy of 0.000 01 g (Sartorius GMBH, Germany) was used for the measurement of endosulfan. All experiments were performed with a stock solution of 200 mg/L, which was prepared afresh after every 10 days. In order to avoid degradation of endosulfan, the stock solution was kept under refrigeration. Endosulfan samples of required concentrations were prepared by adding the stock solution to distilled water (Yedla and Dikshit 2008). The distilled water used for experimentation was prepared in the laboratory and had hardness of 9.8 mg/L as $CaCO_3$, chlorides at 4.5 mg/L, conductivity of 4 $\mu S/cm$, and the endosulfan concentration was not in the range of detection.

Extraction of Endosulfan

Representative samples (30 mL) of aqueous solution spiked with endosulfan were extracted by liquid-liquid partition in a 125-mL separating funnel using *n*-hexane. Extraction was done three times with 10, 10, and 5 mL of *n*-hexane, respectively. During the extraction process, the sample-hexane mixture was shaken for 5 min and then allowed to settle for 5 min. The separated layer of *n*-hexane was passed through a 10-mm bed of sodium sulfate to absorb any trace moisture present in the extracted sample. Hexane extract was collected in a volumetric flask and made to 25 ml with *n*-hexane to make up the hexane lost by evaporation during the transfer of solvent. The extracted sample was analyzed by GC and the concentration of endosulfan was determined.

Preparation of WC

WC, which was obtained from the local market at a price of Rs. 5 per kg (US$=46 Indian Rupees), was pulverized and sieved to get a mean size of 200 μm using Indian standard sieves (a set of Indian standard sieves was used and arithmetic mean methods were employed to arrive at a specific particle size). The sieved adsorbent was washed thoroughly with distilled water and dried at 110°C for 10 h, which was subsequently cooled down to room temperature. This was done to get rid of foreign matter, impurities, and unwanted moisture. WC was then treated with 1-N HNO_3 in order to increase the available surface area for adsorption. [The characteristics of WC measured by means of electron microscopy revealed that it has a honeycomb structure, which facilitated enhancing the available surface area for adsorption by means of acid treatment. Normality of acid determines the extent of corrosive action and hence the possible increase in surface area available for adsorption. More information on this can be obtained from Yedla and Dikshit (1999b).] About 10 g of WC were added to different glass beakers (500-mL capacity) containing 300 ml of 1-N nitric acid solution. The mixtures were agitated under medium speed (40–50 rpm) using a jar test apparatus for 3 h. After the reaction time, WC was separated from the solutions and washed thoroughly with tap water, and then with distilled water until the conductivity of the washed water was found around 4 $\mu S/cm$. After washing, the WC was oven dried for 10 h at a temperature of 110°C to remove the unwanted moisture. It was then cooled to the room temperature, sieved to 200 μm, and stored in airtight bottles for use in further experimentation [as explained by Yedla and Dikshit (2008)]. Treated WC was used throughout the experimentation and is abbreviated as WC. Readers may please note that, from this point onward, both WC and "wood charcoal" represent 1-N HNO_3 treated WC.

Methodology

Adsorption Studies

Distilled water was used for all the batch sorption experiments at room temperature. A mechanical rotary shaker was used to agitate samples in order to ensure a uniformly mixed batch reactor environment. An agitation speed of 150 ± 5 rpm was maintained in all experiments to keep the adsorbent in suspension. Tarson bottles made of polyethylene, of capacity 125 ml, were used for all batch experiments. A number of bottles with 100-ml endosulfan spiked water sample in each, along with the adsorbent at a predetermined dose, were used in each experiment. Bottles were withdrawn from the system after the required contact time, and the sorbent was separated by gravity. A representative sample was then taken from the supernatant of each bottle and analyzed for endosulfan. Polyethylene bottles, before each experiment, were equilibrated with an endosulfan spiked solution to avoid the in-

J. Environ. Eng., 2010, 136(10): 1096-1104

terference of "hydrophobic induced" sorption of endosulfan onto the inner surface of the bottle (Yedla and Dikshit 2008). A control sample (without any WC dose) was also analyzed with each set of experiments to avoid deviations in experimental results. Experiments were repeated as when it was required based on the behavior of the control sample. If the endosulfan concentration on the control sample shows some deviation, then that particular experiment was repeated in order to avoid any error in the experimentation. Therefore, no error bars are presented while reporting the experimental result [as explained by Yedla and Dikshit (2008)].

The following sections present the methodology followed in the experiments to determine the effect of coexisting pesticides, their competitive sorption, and the effect of various external parameters such as pH, ionic strength chlorides, presence of calcium and magnesium, fertilizers, and dissolved organic matter (DOM).

Effect of Coexisting Pesticides (Atrazine and Monocrotophos)

Endosulfan spiked water samples of 100 ml each were taken in eight bottles, and WC was added to each of them at a dose of 10 g/L. Atrazine was then added to the samples at doses of 0.1, 0.25, 0.5, 0.75, 1, 2, and 3 mg/L, respectively, and one sample bottle was a control sample without any atrazine dose. Initial endosulfan concentration was maintained at 1 mg/L in all eight sample bottles. The samples were shaken for 5 h at 150 rpm and then analyzed for residual endosulfan. Control sample was also analyzed for residual endosulfan concentration. The same methodology was followed to study the effect of monocrotophos with the same range of monocrotophos concentrations.

Competitive Sorption of Pesticides

Distilled water samples of 100 mL each were taken in 11 bottles. Endosulfan, atrazine, and monocrotophos were added to every bottle at a concentration of 1 mg/L each. WC was then added to each bottle at a dose of 10 g/L. The sample bottles were agitated at 150 rpm, keeping all other experimental conditions constant. Samples, at a regular interval of 30 min, were analyzed for residual concentrations of endosulfan, atrazine, and monocrotophos.

Effect of External Parameters on Endosulfan Sorption onto WC

The following methodology was adopted for all the experiments designed for delineation of effects of various water quality parameters on endosulfan sorption onto WC. Distilled water samples of 100 ml each were taken in Tarson bottles, spiked with 1-mg/L endosulfan and 10 g/L of WC, and agitated at a constant speed of 150 rpm. After shaking for 5 h the samples were withdrawn and analyzed for residual endosulfan concentrations. A control sample containing only endosulfan and WC was also analyzed for all the experiments. While examining the effect of water quality parameters, all the process parameters such as initial sorbate concentration, adsorbent size and dose, temperature, pH, agitation speed, and agitation time were kept constant. In all the experiments (except for the effect of pH) pH of the sample was adjusted to neutral range by adding 0.1-N NaOH.

Effect of pH. The effect of pH on sorption of endosulfan was studied at different pH values ranging from 2.2 to 11. Samples were adjusted for pH by adding either 0.1-N NaOH or 0.1-N HCl. The initial and final pH values were analyzed using a digital pH meter.

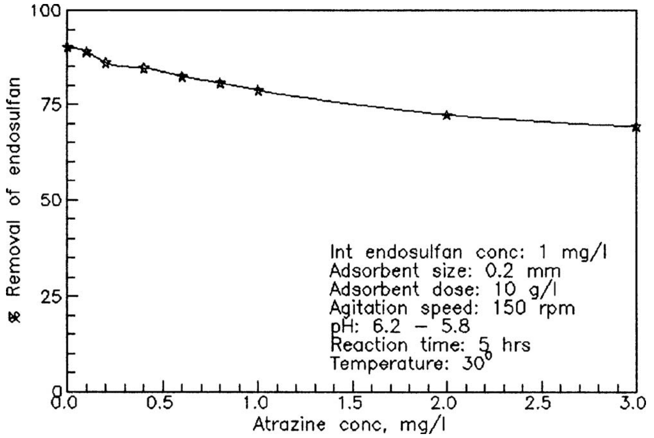

Fig. 1. Effect of atrazine concentration on the adsorption of endosulfan onto WC

Effect of Ionic Strength and Chloride Concentration. The effect of ionic strength on the removal of endosulfan was studied over a range $10^{-4}–10^{-1}M$ using varying doses of $NaNO_3$. The effect of chloride concentration (as Cl^-) was studied by adding NaCl in a range 0–200 mg/L.

Effect of Calcium and Magnesium Ions. The effect of Ca^{+2} and Mg^{+2} ions on the sorption of endosulfan was studied individually, for concentration ranges 0–110 and 0–124 mg/L, respectively. The initial and final concentrations of Ca^{+2} and Mg^{+2} ions were analyzed using a flame emission atomic absorption spectrophotometer. $Ca(NO_3)_2$ and $MgSO_4$ were used for maintaining the Ca^{+2} and Mg^{+2} concentrations, respectively.

Effect of Fertilizers. The effect of urea and single superphosphate (SSP) was studied in the concentration ranges 0–130 and 0–100 mg/L, respectively. Commercially available urea and SSP were used to study their effect on endosulfan sorption onto WC.

Effect of DOM. Humic acid and polyacrylic acid were considered as DOM in water. The influence of DOM on endosulfan sorption onto WC was studied in the concentration ranges of 10, 20, 30, and 40 mg/L of DOM (humic and polyacrylic acid separately).

Results and Discussion

Effect of Coexisting Pesticides

Wide varieties of pesticides are in use for agriculture, and their residue reaches water streams by means of agriculture runoffs. Thus, it is very likely that more than one pesticide exist in the water streams. Adsorption efficiency of WC may be affected by the coexisting pesticides as they compete for the limited adsorption sites available in the reactor. Atrazine and monocrotophos, weedicide and insecticide, respectively, are among the widely used pesticides in conjunction with endosulfan. Hence, the effect of atrazine and monocrotophos on sorption of endosulfan onto WC was studied in this section.

Fig. 1 presents the effect of atrazine on endosulfan sorption

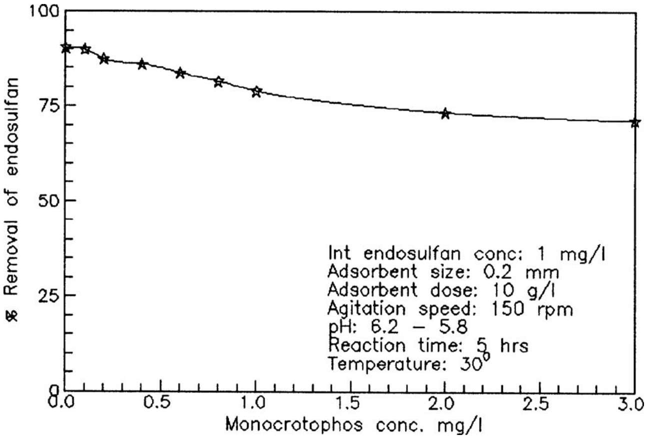

Fig. 2. Effect of monocrotophos concentration on the adsorption of endosulfan onto WC

onto WC. Increasing concentration of atrazine in water seems to have increased the hindrance effect on endosulfan sorption onto WC. Hindrance, as high as 20% of endosulfan uptake, was observed at an atrazine concentration of 2 mg/L. The hindrance effect was rapid up to 2 mg/L of atrazine concentration and then it became asymptotic to the *x* axis. The presence of monocrotophos has also showed a similar effect on endosulfan adsorption onto WC, which is shown in Fig. 2. Given that atrazine and monocrotophos represent two varying categories of pesticides, one a herbicide and the other organoprosperous insecticide, it may be plausible to claim that endosulfan adsorption onto WC gets hindered by about 20% in the presence of coexisting adsorbates.

The molecular weights of endosulfan, atrazine, and monocrotophos are 406.96, 215.7, and 223.2, respectively. While many factors such as molecular size, molecular structure, and affinity to adsorbent could play a significant role in limiting adsorption among multiple sorbates (Weber 1972), competitive sorption due to hydrophobic nature of adsorbates could be more likely reason for the observed hindrance effect of atrazine and monocrotophos on endosulfan sorption onto WC. The difference in the concentration gradients of endosulfan and the other two competing pesticides could also play an important role in the hindrance effect. At 1-mg/L concentrations of competing adsorbate, which is at the same level as of endosulfan, the hindrance is not significant. As the concentrations of competing sorbates became double that of endosulfan, maximum hindrance effect was observed. This further supports the argument that concentration gradient could be controlling the hindrance effect.

Competitive Sorption of Pesticides

Review of the existing literature has clearly revealed that the presence of more than one pesticide in water streams is very common. A brief field survey revealed that endosulfan, monocrotophos, and atrazine are the most commonly used pesticides in their order of mention. While the presence of other pesticides affect endosulfan uptake onto WC, it is essential to study the competition among all pesticides for the adsorbent space. This would present an indicative loss of capacity for endosulfan sorption onto WC.

In an experiment to estimate the competitive adsorption, all three pesticides, namely, endosulfan, atrazine, and monocrotophos, were added to the sample at an equal dose of 1 mg/L each, and adsorption process was carried with WC at a dose of 10 g/L. The analysis of all three pesticides at an interval of 30 min is presented in Fig. 3. Endosulfan sorption onto WC has dominated the process followed by atrazine and monocrotophos, respectively. As presented in Fig. 4, endosulfan was adsorbed onto WC by 75% followed by atrazine (45%) and monocrotophos (39%). Endosulfan uptake onto WC was reported to be 95% under the similar experimental conditions (Yedla and Dikshit 1999b). Hence the loss of endosulfan uptake due to competitive adsorption among the three pesticides is in the order of 20%.

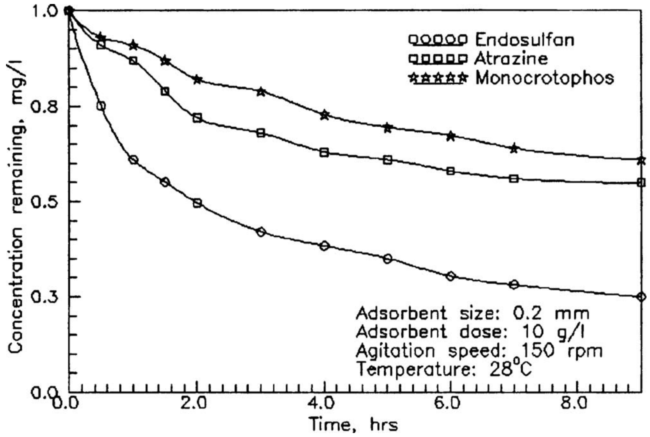

Fig. 3. Sequential uptake profiles of atrazine, endosulfan, and monocrotophos

Saturation adsorption capacity of WC for endosulfan was reported to be 0.53 mg of endosulfan onto 1 g of WC (Yedla and Dikshit 1999a). In the competitive sorption experiment it was found that endosulfan uptake capacity stands at 0.07 mg per 1 g of WC. It is as less as 15% of the original adsorption capacity. Total adsorbate uptake (endosulfan, atrazine, and monocrotophos together) was found to be 0.16 mg over 1 g of WC, which is just 30% of the original saturation adsorption capacity of WC. From this it is clear that coexisting pesticides hinder the performance of endosulfan sorption onto WC to a great extent.

From literature it is clear that hydrophobity along with the molecular weight and structure drives the sequence of uptake in adsorption. Usually more hydrophobic molecules are susceptible to greater sorption over the nonpolar sorbents (Moore and Ramamoorthy 1984; Weber 1972; Keerthinarayana and Bandyopadhyay 1993). The molecular weights of endosulfan, atrazine, and monocrotophos are 406.96, 215.7, and 223.2, respectively, and water solubility at 20°C stands at 0.32 mg/L (endosulfan), 33 mg/L (atrazine), and 1,000 mg/L (monocrotophos). Based on their respective solubilities, endosulfan is more hydrophobic than atrazine, which is more hydrophobic than monocrotophos. It is prob-

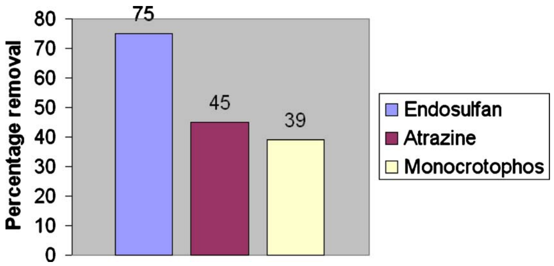

Fig. 4. Sequential uptake of atrazine, endosulfan, and monocrotophos onto WC

J. Environ. Eng., 2010, 136(10): 1096-1104

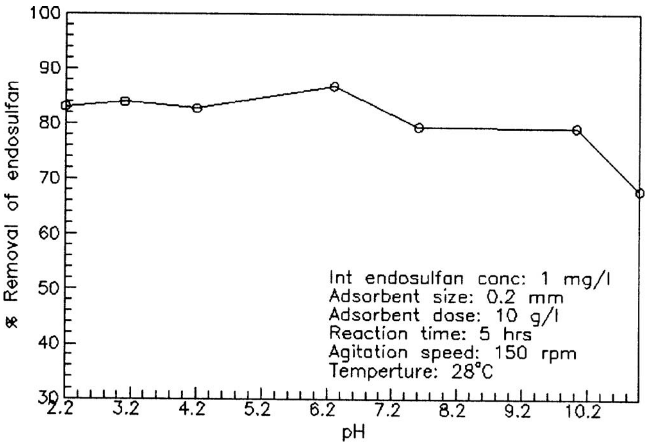

Fig. 5. Effect of pH on endosulfan removal using WC

ably these hydrophobic forces that control the order of uptake (as presented in Figs. 3 and 4) of the three pesticides onto WC. As monocrotophos is more hydrophilic in nature it did not compete hard for the available adsorption sites on WC and hence resulted in less uptake. From this study it can be concluded that when endosulfan, atrazine, and monocrotophos are present in water, the order (percentage) of their uptake onto WC would be endosulfan, atrazine, and monocrotophos.

Effect of External Parameters

Effect of pH and Ionic Strength

For any treatment process such as adsorption and ion exchange, pH of the adsorbate, adsorbent, and the system as a whole has a significant influence on the efficiency. The effect of pH on endosulfan sorption onto WC is shown in Fig. 5. Change in percentage sorption in acidic environment was found insignificant. Maximum sorption of endosulfan was observed at a pH of 6.3. Percentage sorption of endosulfan had decreased from 87 to 79% as pH increased to 7.6. It further reduced to 68% as pH increased to 11. However, the change was observed mostly after pH reached 10.

Both sorbate and sorbent may have chemical characteristics, which are affected by the concentration of hydrogen ion (H^+) in the solution. Some sorbents may have affinity for H^+ or OH^- ions and can directly affect the pH of the solution and therefore solubility and sorption capacity (Slejko 1985). In general, the H^+ and OH^- ions affect the absorption process through dissociation of functional groups on the adsorbate and adsorbent (Weber and Morris 1963). Treated WC in an aqueous phase along with endosulfan revealed a marked affinity for OH^- ions than H^+ ions, and this was confirmed by the change in pH of the solution from 6.4 to 5.8. The variation of pH at different initial pH values is shown in Table 1. A decreasing trend of percentage sorption in both acidic and alkaline environments was observed with lindane removal (Keerthinarayana and Bandyopadhyay 1993). A similar trend was observed in sorption of DDT and sevin (1-naphthyl ester of *N*-methyl carbamic acid, a carbamate pesticide) from aqueous phase (Keerthinarayana et al. 1989; Shivalingaiah et al. 1989).

Zero point charge pH (pH_{ZPC}) can be used to interpret the effect of pH on endosulfan removal efficiency. pH_{ZPC} is the pH that adsorbent imparts to the solution at zero point charge and is used to explain the effect of pH on the sorption process. pH_{ZPC} facilitates explaining the mechanism with distinction for both sorbate and sorbent charges (Bhattacharya and Venkobachar 1984). As per the procedure outlined by Haung and Ostavic (1978) the pH_{ZPC} of WC was found to be 5.65 (Yedla 1999). This value lies within the range of pH_{ZPC} values 4.9–7.8 obtained for different activated carbons by Haung and Ostavic (1978).

Table 1. Variation of pH at Different Initial pH Values

Initial pH (1)	Final pH (2)	Release of H^+ or OH^- (3)
2.20	2.36	0.16 (OH^-)
3.10	3.20	0.10 (OH^-)
4.20	4.22	0.02 (OH^-)
6.30	4.70	1.60 (H^+)
7.60	5.26	2.34 (H^+)
10.03	6.45	3.58 (H^+)
11.00	7.60	3.40 (H^+)

For $pH < pH_{ZPC}$, WC surfaces possess positive charge and when $pH > pH_{ZPC}$, negative charge. Though endosulfan is nonionic in nature, the terminal hydrogen in the molecule plays a significant role in the sorption process. The maximum percentage of sorption was obtained at a pH of 6.3. When WC is negatively charged, the attraction between the positive charge on the terminal hydrogen in the endosulfan molecules and the negative charge on WC could be the reason for attaining maximum efficiency. As OH^- concentration increases, endosulfan gets hydrolyzed to endosulfan diol (after a pH of 10). Repulsion between OH^- ions and terminal OH in endosulfan diol may be the reason for drastic decrease in efficiency after a pH of 10. As discussed in the previous paragraph, the uptake of H^+ and OH^- ions was also responsible for the reduction in endosulfan sorption.

Overall distribution of natural compounds, including pesticides onto the natural materials such as activated charcoal, WC, etc., was found to be affected by the ionic strength of aqueous phase (Briggs 1981). Though the general trend of the ionic strength of natural waters is $10^{-3}M$, in the present study the effect of ionic strength on endosulfan sorption onto WC was studied in a range $0.1-10^{-4}M$. The effect of ionic strength as equivalent of $NaNO_3$ is shown in Fig. 6. It depicts that ionic strength had no effect on endosulfan sorption onto WC except at $0.1M$ where a slight reduction in sorption was observed. This result of quite an expected behavior as endosulfan is nonionic at neutral conditions.

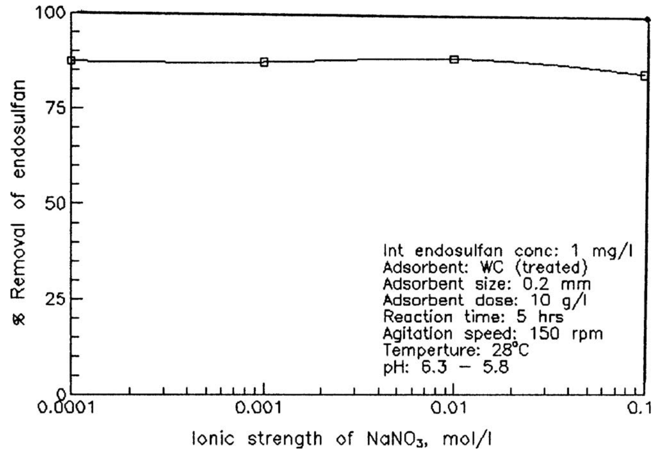

Fig. 6. Effect of ionic strength on the adsorption of endosulfan onto WC

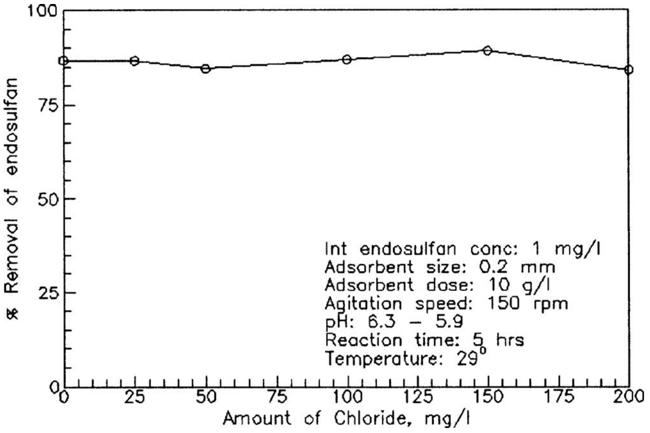

Fig. 7. Effect of chloride concentration on the adsorption of endosulfan onto WC

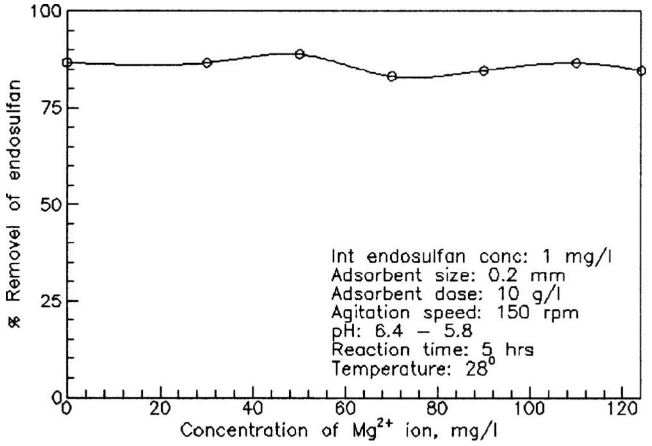

Fig. 9. Effect of Mg^{2+} ion concentration on the adsorption of endosulfan onto WC

Effect of Chloride Concentration

The effect of Cl^- concentration on the sorption of endosulfan onto WC was tested in a range 0–200 mg/L and shown in Fig. 7. The limit of chloride concentration in natural waters is 200 mg/L. Fig. 7 explains that the effect of chloride concentration on endosulfan sorption is insignificant up to 150 mg/L. As the chloride concentration increased to 200 mg/L the endosulfan sorption was reduced by 6% compared to the base case of endosulfan sorption onto WC. This reduction in adsorption capacity is almost insignificant and hence not a major concern. Blocking of hydrophobic adsorption sites on WC by Cl^- could be the possible reason for such a fall in endosulfan sorption.

Effect of Ca^{2+} and Mg^{2+}

The effect of Ca^{2+} and Mg^{2+} on sorption of endosulfan onto WC was found out in a wide range of concentrations. Ca^{2+} was studied in a range 0–110-mg/L concentrations whereas Mg^{2+} was studied for a range 0–124 mg/L. The results were shown in Figs. 8 and 9. Ca^{2+} at a concentration of 10-mg/L reduced endosulfan sorption by 8%, and the effect stands insignificant at all other doses. The effect of Mg^{2+} remained largely insignificant except at a concentration of 90 mg/L where efficiency of endosulfan sorption onto WC had reduced by 2%. Both Ca^{2+} and Mg^{2+} appear to be competing with endosulfan for the available adsorption sites on WC, and that could be the reason for that sporadic loss of efficiency in endosulfan sorption. These fluctuations in sorption efficiency may be due to electrostatic attraction between these cations and the negatively charged sites on WC surfaces (since at $pH > pH_{ZPC}$, WC possesses a negative charge), fast diffusion of these cations having small hydrated radii into the pores of WC as compared to molecular diffusion of endosulfan, and the binding of cations with mixed clayey minerals in WC (though they are less in concentrations). However, as the effect is almost insignificant, their presence would not influence the design of adsorber system for the removal of pesticides from drinking water.

Effect of Urea and SSP

In agriculture, fertilizers are used along with pesticides. Particularly in modern agricultural practices, the use of excess fertilizers has become extremely common. Most of the synthetic fertilizers used in agriculture worldwide are either nitrogenous or phosphatic compounds. The use of excess fertilizer leads to pollution of surface waters. They also seep through soils to pollute groundwaters. In view of the unavoidable presence of fertilizers in natural waters, their impact on the performance of WC in adsorbing endosulfan is important and hence included in this study. Commonly used fertilizers, namely, urea (fertilizer grade, 45% N_2) and SSP (fertilizer grade, 10% P_2O_5), are considered as representative compounds for this study. Figs. 10 and 11 present the effect of

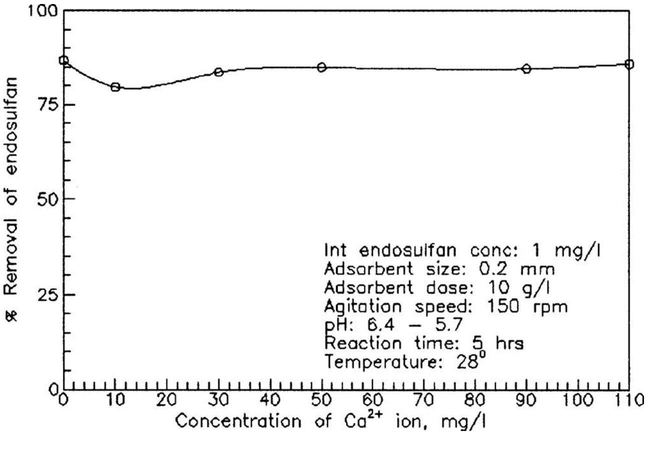

Fig. 8. Effect of Ca^{2+} ion concentration on the adsorption of endosulfan onto WC

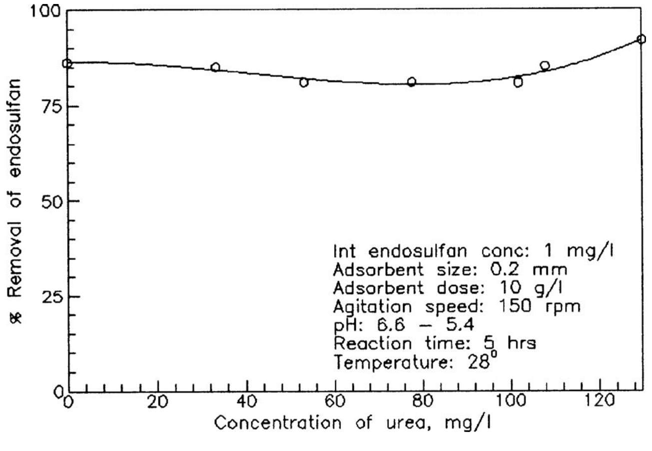

Fig. 10. Effect of urea on the adsorption of endosulfan onto WC

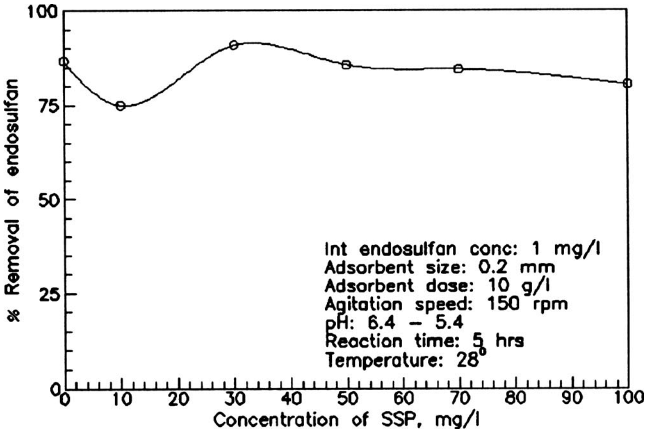

Fig. 11. Effect of SSP on the adsorption of endosulfan onto WC

urea and SSP on endosulfan sorption onto WC.

The efficiency of endosulfan sorption onto WC had decreased by 6% in the presence of urea at a concentration range 33–102 mg/L. However, the sorption efficiency has increased by 17% at a urea concentration of 130 mg/L. Urea is a highly water-soluble and acid forming compound. It gets hydrolyzed to ammonium carbonate at a very fast rate when added to water

$$CO(NH_2)_2 + 2H_2O\Phi(NH_4)_2CO_3 \tag{1}$$

Ammonium carbonate is an unstable compound and decomposes to NH_4^+ and CO_2. As urea concentration increases the pH of solution decreases (Keerthinarayana and Bandyopadhyay 1993). In this process, it not only reduces the pH of the solution but also hydrolyzes endosulfan to endosulfan sulfate ($C_9H_6Cl_6O_4S$). At a urea concentration of 130 mg/L, there could be considerable hydrolysis of endosulfan to endosulfan sulfate. This could be the reason for the fall in measured endosulfan concentration in water.

At a concentration of 10 g/L, SSP resulted in decreasing the sorption efficiency of endosulfan onto WC by 13%, which was later found to be recovering at a concentration of 30 g/L. Over a range of concentrations, SSP appeared to be insignificant in affecting the sorption efficiency of endosulfan onto WC. SSP has two parts of monocalcium phosphate and three parts of gypsum by weight. Reduction in sorption efficiency of endosulfan into WC is mainly due to the presence of Ca^{2+} ions competing for the adsorption sites on the surface of WC.

Effect of DOM

The presence of greater variety of natural and synthetic organic matters such as humic acid, fulvic acid, amino acids, polyacrylic acid, and other chemicals from nonpoint sources in natural and aquatic environments is common. The association of chlorinated compounds such as dieldrin and pentachlorophenols with natural organic matter such as humic acid and fulvic acid is well documented (Faust and Hunter 1971; Carter and Suffet 1982). Hence, the effect and interaction of these background organics with hydrophobic pesticides are considered as an essential factor while developing an adsorbent to remove pesticides from water environment. Therefore, the effect of cosolutes such as humic acid and polyacrylic acid on the removal of endosulfan at different concentrations was studied, and the results are shown in Figs. 12 and 13.

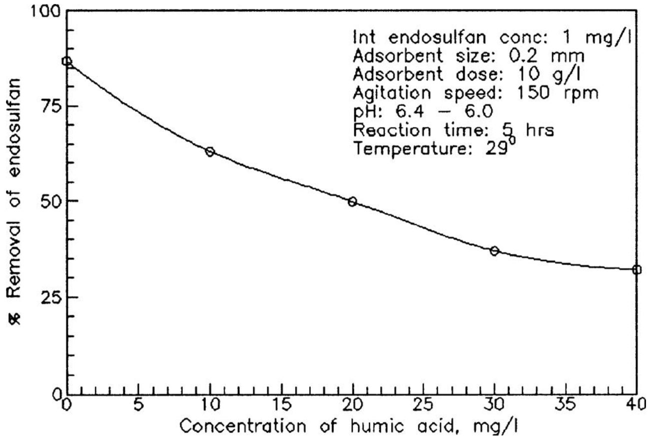

Fig. 12. Effect of humic acid on the adsorption of endosulfan onto WC

Humic acid has shown a significant impact on endosulfan sorption efficiency onto WC. Within a concentration range 0–40 mg/L it has reduced the sorption efficiency of endosulfan onto WC by 55%. In similar studies earlier, Pirbazari and Weber (1984) and Pirbazari et al. (1991) reported that the removal efficiency of dieldrin, alachlor, and heptachlor by activated carbon was adversely affected by background organic substances such as humic acids. More solubility of any organic matter in aqueous phase results in its poor sorption (Sawyer and McCarty 1978). The partitionlike interaction of the solute with the "microscopic organic environment" of dissolved humic molecules would be a reasonable explanation for solute solubility enhancement (Chiou et al. 1986). The extent of solubility enhancement and/or specific interaction with hydrophobic chlorinated pesticides depends on the type of DOM, its concentration, and source of DOM (Chiou et al. 1986). The reduction in the efficiency of endosulfan sorption onto WC could be mainly attributed to the apparent solubility enhancement of endosulfan by humic acid molecules as explained above. More solubility enhancement of endosulfan by commercial humic acid was expected relative to natural humic materials on account of its higher content of nonpolar molecular moieties.

Humic acid and other background organics, along with endosulfan, compete for the available adsorption sites on WC, and this competitive sorption could also play a role along with the decreasing hydrophobic character of endosulfan (due to the increased solubility) due to the presence of humic substances, in reducing the sorption efficiency for endosulfan. The effect of

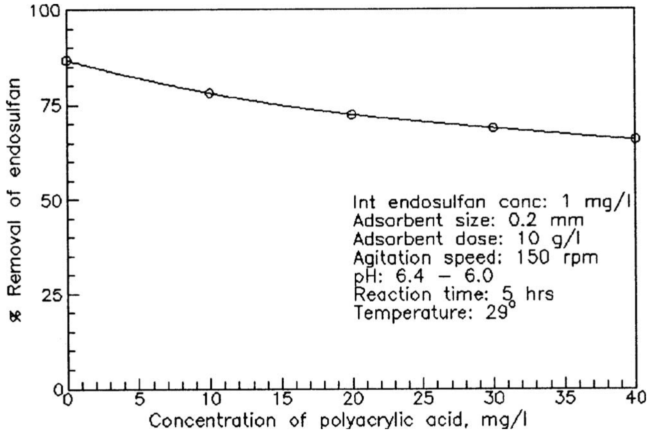

Fig. 13. Effect of polyacrylic acid on the adsorption of endosulfan onto WC

J. Environ. Eng., 2010, 136(10): 1096-1104

polyacrylic acid on the removal efficiency of endosulfan onto WC is less significant compared to that of humic acid.

Summary and Conclusions

In a study carried out to find the effect of coexisting pesticides, viz., atrazine and monocrotophos on endosulfan sorption onto WC, both atrazine and monocrotophos showed an increasing trend of inhibition with the increase in their initial concentrations.

- Competition among pesticides for the available adsorption sites on WC was found to follow the order as endosulfan $>$atrazine$>$monocrotophos. Overall uptake capacity of WC in the presence of cosorbates has reduced significantly.

The removal of endosulfan by using WC was found affected by various external parameters and other coexisting elements.

- Endosulfan adsorption was affected at high pH values where endosulfan turns ionic. In a lower range of pH endosulfan sorption onto WC remained unchanged. Ionic species does not seem to affect the adsorption of endosulfan as expected, as endosulfan is nonionic (pH=6) under neutral conditions. The effect of ionic strength was studied in the range $0.1-10^{-4}M$ and there was no significant effect on endosulfan removal.

The effect of chlorides was insignificant except at a concentration of 200 mg/L. Ca^{2+} and Mg^{2+} did not show much effect except for small variations at a short range of concentrations.

The effect of urea (fertilizer grade, 45% N_2) and SSP (fertilizer grade, 10% P_2O_5) was determined separately at concentration ranges 0–120 and 0–110 mg/L, respectively.

- Urea had affected the efficiency at a concentration range 60–100 mg/L. In case of SSP the effect was even higher.
- Among the dissolved organic content, humic acid was found inhibiting the WC performance more significantly (55% reduction in efficiency) than that of polyacrylic acid. Competitive sorption could be the reason for the reduced efficiency of endosulfan removal in the presence of these competing elements.

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