SORPTION AND DESORPTION OF 2,4-D AND ATRAZINE FROM WATER ENVIRONMENT BY WASTE TYRE RUBBER GRANULES AND ITS MANAGEMENT

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ABSTRACT

Waste tyre rubber granules were used as sorption medium in water treatment technology to remove up to 1 mg l^{-1} of 2,4-D and atrazine. The removal was found to be 83.2% and 87% corresponding to initial concentration of 0.5 and 1 mg l^{-1} of 2,4-D whereas it was 84.2% and 87.6% for atrazine. On the basis of solubility of specific solution and adsorption interaction, 15% ethyl alcohol and 15% acetone solutions were found to be effective as regeneration solvents for 2,4-D and atrazine, respectively. Even after three cycles of sorption and regeneration, rubber granules had significant residual adsorption capacity; hence it could be reused over many more cycles of operation. Finally, exhausted waste tyre rubber granules were effectively disposed by mixing it with asphalt.

KEYWORDS: Tyre Granules, 2,4-D, Atrazine, Ethyl alcohol, Acetone.

INTRODUCTION

Sustainable use of an adsorbent is prime issue in evaluation of suitability of a new adsorbent. An adsorbent will fail in practice if it can not be regenerated and hence, reused. If an adsorbent can be regenerated, then it can be used repeatedly for adsorption. When its removal capacity falls below 50%, it can be disposed off safely. The disposal of spent adsorbent is also a very important concern particularly when it comes under hazardous material category; as environmental regulatory authorities have formulated many rules and regulations on hazardous materials disposal. Generally most of the waste tyres are either land-filled or incinerated. These methods are, however, not appropriate to handle waste tyre because these result in environmental problem such as air pollution or tyres tend to float to surface over time. In attempt to use low cost material, the use of tyre rubber as a sorbent has been investigated for removal of heavy metals, hydrogen sulfide, ammonia and volatile organic compounds (Park and Jhung, 1993; Scheels and Park, 1995). Waste tyre rubber granules were also found to be effective for removal of non-ionic surfactant from water environment (Shalaby and Feky, 1999). Mahramanlioglu *et al.* (1997) reported that activated carbon produced from tyres could be used as adsorbent for organic pollutants while Kim *et al.* (1997) directly used waste tyre rubber granules for removal of toluene, methanol etc. from water environment and found it to be effective. In their earlier work, Alam *et al.*

(2000) had shown that rubber granules can be selected as the appropriate sorbent for removal of 2,4-D and atrazine from the water environment to the WHO drinking water quality standard of 20 μg l^{-1} for 2,4-D and 3 μg l^{-1} for atrazine. The present paper discusses the detailed evaluation of sorption and desorption behaviour of rubber granules to remove 2,4-D and atrazine from water environment including the procedure for disposal of exhausted sorbent.

METHODOLOGY
Determination of 2,4-D and Atrazine
All the reagents used were of analytical grade. All glassware used was of Borosil. Distilled water was used for making synthetic samples. Before each experiment, all glassware were cleaned with dilute nitric acid and repeatedly with distilled water followed by drying at 110^{0}C for 5 hrs. Technical grade 2,4-D of 95% purity was obtained from Vijayalakshmi Insecticides, India. Diethyl ether and toluene of 99.9% purity were used for the determination of 2,4-D by Gas Chromatography (GC).

Technical grade atrazine of 98% purity was obtained from Rallis India Ltd. For analysis of atrazine, ethyl acetate of 99.9% purity was used for Gas Chromatography and dichloro methane of 98% purity was used for UV-Visible spectrophotometeric method.

Analytical Methods
Standard methods (APHA-AWWA-WPCF, 1989) were adapted for the analysis of various water quality parameters. Shimadzu (Japan) Gas Chromatograph model GC-14A was used for the measurement of both 2,4-D and atrazine. Electron Capture Detector (^{63}Ni) with 5% OV-17 stainless steel porapak packed column was used. The column was of 3 m length and 3.18 mm (1/8$^"$) diameter. For 2,4-D, temperatures for column, injector, and detector were maintained at 195°C, 250°C, and 300°C, respectively while the same were kept as 215°C, 220°C and 265°C, respectively for atrazine. Nitrogen gas having 99.9% purity was used as carrier gas. Its flow rate was maintained as 50-60 ml min^{-1} for 2,4-D and 80-90 ml min^{-1} for atrazine. Before the actual measurements, the GC was conditioned for 48 hours to avoid column bleeding and soiling of sample and to maintain ideal conditions for every GC run.

Atrazine measurements were also cross-checked using Shimadzu (Japan) UV-Visible spectrophotometer model UV 3100 at 229 nm after the extraction of sample using dichloro methane.

Sample Preparation
Stock solution of 2,4-D was prepared in distilled water while stock solution of atrazine was prepared by dissolving atrazine in acetone. All experiments were performed with a stock solution of 200 mg l^{-1}, which was prepared afresh after every 10 days. The samples of required concentrations were prepared by diluting the stock solution with distilled water. Preparation of rubber granules as sorbent was carried out procedure outlined in Alam et al. (2000).

Extraction of 2,4-D and Atrazine
The quantification the concentration of 2,4-D or atrazine by GC requires its extraction from aqueous phase onto a suitable organic media. 2,4-D was extracted from the representative sample (100 ml) of aqueous solution containing 2,4-D by liquid-liquid partition in a 125 ml separating funnel using diethyl ether. The extraction was done three times with 10 ml, 10 ml, and 5 ml of diethyl ether, respectively. During the extraction process, the sample-diethyl ether mixture was shaken for 5 min and then allowed to settle for 5 min. The separated layer of diethyl ether was passed through a 10 mm bed of sodium sulphate to absorb any trace moisture present in the extracted sample. Then diethyl ether extract was collected in a volumetric flask and evaporated to dryness and esterified by BF$_3$-methanol and made to 25 ml with toluene (APHA-AWWA-WPCF, 1989). The extraction efficiency of diethyl ether was found out by measuring 2,4-D in three samples of known concentration by GC. The extraction efficiency was found to be 80-87% and is comparable to that found by Grover *et al.* (1985). The extraction of atrazine from aqueous solution was also done in same manner as outlined above but ethyl acetate was used as the solvent. The extraction efficiency was found 90%-95%.

Sorption Kinetics
All batch sorption experiments were carried out using synthetic samples in distilled water at room temperature in mechanical shaker (S.C. Dey & Co., Calcutta, India). A medium agitation speed of about 140 to 150 rpm was maintained to keep the sorbents in suspension during the experimental studies to simulate as equivalent completely mixed batch reactor (CMBR). Polyethylene bottles (Tarson Co. Ltd., India) of

250 ml capacity containing a reaction mixture of 200 ml solution spiked with known concentration of herbicides 2,4-D and atrazine were used with known amount of rubber granules in each test. The bottles were withdrawn from the system after the required reaction time and sorbent was separated by gravity filtration. Representative samples (100 ml) of were taken from the bottles, extracted and analyzed for respective herbicides as per the method outlined in earlier sections.

The sorption kinetics experiments were carried out using different initial concentration of 1 mg l^{-1} and 0.5 mg l^{-1} of 2,4-D or atrazine containing 23 g l^{-1} rubber granules of 150-300 μm size as sorbent.

Batch Study for Selection of Solvent for Regeneration

For selection of suitable solvent solution for regeneration, plastic bottles containing 1.8 g of rubber granules and 100 ml of specific solvent solution for regeneration were used in batch study. A medium agitation speed of about 150 rpm was maintained to keep the sorbent in suspension during the experimental studies. The bottles were withdrawn from the system after the required reaction time and the sorbent was separated by gravity filtration. The residual 2,4-D and atrazine in filtrate was measured. Based on literature, 15% ethyl alcohol solution and 15% toluene solution for 2,4-D and 15% acetone solution and 15% toluene solution were used for atrazine, respectively, as candidate solvents.

Batch Sorption, Desorption and Regeneration Test

1.8 g of sorbent was added to different plastic bottles containing 100 ml of distilled water spiked with 4 mg l^{-1} of 2,4-D and atrazine and equilibrated for a reaction time of 3 hr. After the reaction time, the sorbent was separated from the solution and the solution was analyzed for the herbicides. The sorbent was then dried at room temperature and used for the desorption studies. Desorption studies were conducted by 15% diethyl ether and 15% acetone solution for 2,4-D and atrazine, respectively.

Regeneration studies were performed for 3 cycles by using 15% ethyl alcohol and 15% acetone solution for 2,4-D and atrazine respectively. Sorption was carried out using 100 ml of the herbicide-distilled water for 3 hr and then desorption test was carried out by using specific solvent solution for next 6hr. The same procedure was adopted for 2nd and 3rd cycle of operations. For each cycle, the difference of the amount of the herbicide present onto adsorbent after sorption and desorption process was determined.

Column Sorption and Regeneration

Fixed bed studies were performed for waste rubber granules using 2,4-D and atrazine spiked separately with tap water and distilled water. A perplex glass column of an internal diameter of 3 cm was packed with the sorbent of size 150-300 μm for a depth of 25 cm. The bed was sandwiched between the two layers of 2 cm each of pre-equilibrated glass wool to support the bed and to prevent entrance and exit flow disturbances. An initial 2,4-D and atrazine concentration of 2 mg l^{-1} and a flow rate of 0.672 m^3 m^{-2} hr^{-1} (8 ml min^{-1}) in upflow direction were maintained. The influent and effluent samples were collected periodically for the generation of breakthrough curves with the initial concentration 2 mg l^{-1} of herbicides and analyzed for 2,4-D and atrazine separately.

For carrying out desorption study, first fixed bed sorption experiment was conducted as outlined above until the rubber granules became saturated with 2,4-D or atrazine i.e. the C/C_0 ratio reached approximately close to 1. Then, after drying the bed, 15% ethyl alcohol solution was passed at 5 ml min^{-1} in a downward flow pattern for bed saturated with 2,4-D. In case of atrazine, 15% acetone was used as effluent. The effluent samples were collected at regular time intervals were analyzed for 2,4-D or atrazine concentration. After obtaining complete desorption of the herbicides, again column was tested for sorption in the same manner as described above. The adsorption and desorption processes were repeated for two cycles.

RESULTS AND DISCUSSION
Sorption Kinetics

The removal kinetics of 2,4-D and atrazine by the rubber granules for 1 mg l^{-1} and 0.5 mg l^{-1} concentrations are shown in Figures 1 and 2 respectively. It may be seen that more than 60% of the herbicides were sorbed with 60 min of reaction time and this was due to the availability of the number of free sites within rubber granules and a high concentration gradient between the solution and the solid phase. Literature reports the attainment of the equilibrium for sorption of herbicides or pesticides in CMBR to range from few minutes to several hours (Aly and Faust, 1965; Adams and Watson, 1996, Tsezos and
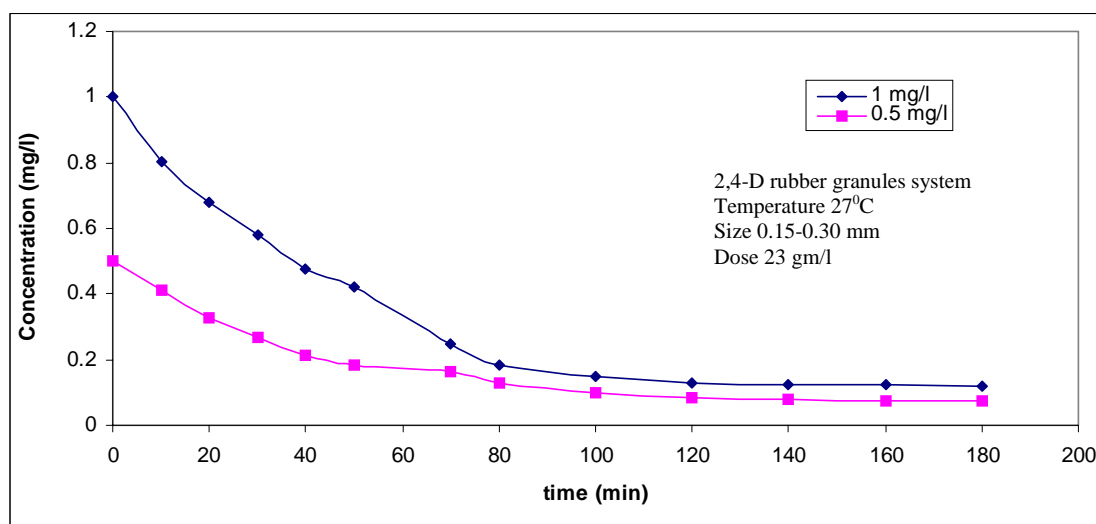
Figure 1.   Change of concentration with time for 2,4-D sorption on rubber granules with initial
                concentration of 1 mg l^{-1} and 0.5 mg l^{-1}

Wang, 1991). In the present study, after 100 min of reaction time, the kinetics profiles gradually became flat indicating the final equilibrium. The removal of both 2,4-D and atrazine beyond 120 min of reaction time was very low and hence an equilibrium time of 120 min was standardized for the rest of the experiments in both the cases. Over this time, the removal was 83.2% and 87% corresponding to initial concentration of 0.5 mg l^{-1} and 1 mg l^{-1} , respectively for 2,4-D whereas the same was 84.2% and 87.6% for atrazine.

Regeneration and Resorption

The possibility of regeneration of loaded rubber granules is crucially important to keeping the process costs down.   In regeneration, the herbicides deposited on rubber granules are washed out (i.e. desorbed) using suitable solvent and rubber granules is regenerated for another cycle of application. Screening of the most effective regenerating solution is very important factor for optimizing the overall operation cost of sorption system from view point of field adaptability.

Solvent dependence of regeneration was examined with the help of following equation proposed by Toman *et al.* (1996) assuming perfect mixing of the herbicides in corresponding solution

$$q = q_0 \exp(-k\{TRTIn(C_s \ / C)\}^2 \qquad (1)$$

where C is the concentration of the herbicide in the solvent, C_s is the solubility of the herbicide in the solvent and parameter k is related to the adsorptive interaction. The efficiency of a solvent for regeneration depends on the value of k and C_s. If k is large or C_s is large, then the amount desorbed is also large.

15% ethyl alcohol solution and 15% toluene solution for 2,4-D and 15% acetone solution and 15% toluene solution were used for atrazine, respectively, as candidate solvents. It was found that for 2,4-D, the solubility of 2,4-D in 15% diethyl ether and 15% toluene were 36.71 g l^{-1} and 1.27 g l^{-1} respectively. The values of k found by least square method for 15% diethyl ether and 15% toluene were 1.03 x 10^{-7} (mol kcal^{-1})^2 and 7.89 x 10^{-8} (mol kcal^{-1})^2 (mol kcal^{-1})^2 respectively. It can be seen that both C_s and k values are higher for 15% diethyl ether than those for 15% toluene indicating diethyl ether to be a better solvent for regeneration for 2,4-D. Similarly, the solubility of atrazine in 15% acetone and 15% toluene were 4.68 g l^{-1} and 0.91 g l^{-1} respectively. The values of k found by least square method for in 15% acetone and 15% toluene were 9.77 x 10^{-8} (mol kcal^{-1})^2 and 8.56 x 10^{-8} (mol kcal^{-1})^2 respectively. Since both C_s and k values are higher for 15% acetone than those for 15% toluene, acetone is better solvent for regeneration for atrazine.
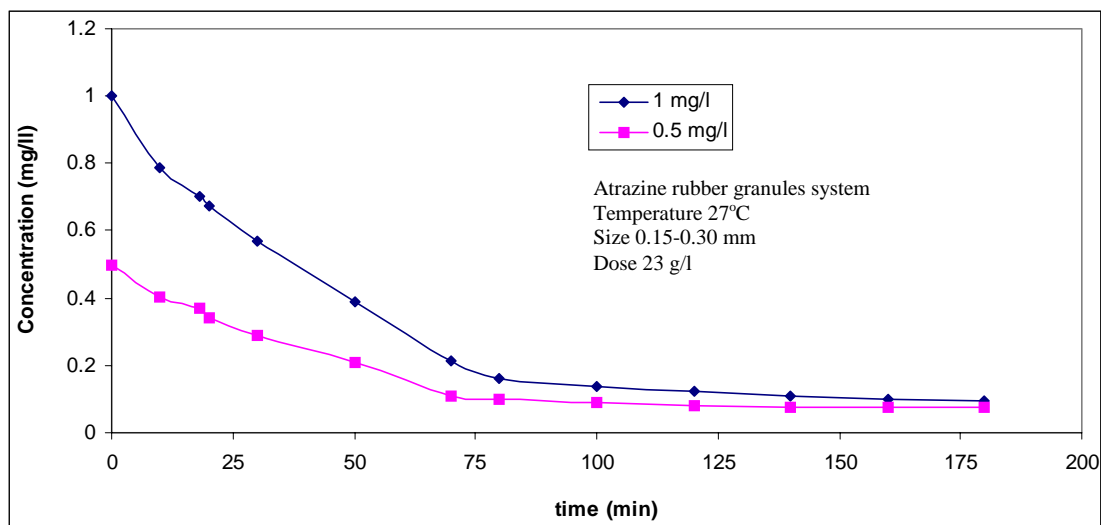
Figure 2. Change of concentration with time for atrazine sorption on rubber granules with initial concentration of 1 mg l^{-1} and 0.5 mg l^{-1}
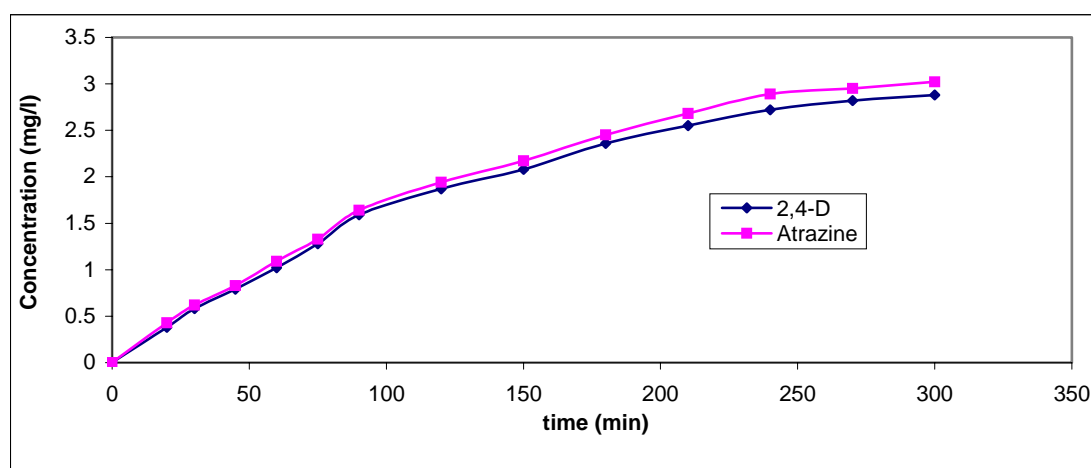

Figure 3. Desorption kinetic profiles for 2,4-D and atrazine desorption in organic solvent media

The desorption of herbicides is due to two reasons: (i) in most cases, the solvating forces developed between solute-solvent partitioning are much greater than the physical sorption forces binding the molecules of the herbicides onto activated carbon of rubber granules; (ii) the greater penetrability of organic solvents into the very fine pores, causes the displacement of the herbicide molecules from the rubber granules. The desorption of 2,4-D and atrazine from exhausted rubber granules was separately undertaken in 15% ethyl alcohol solution and 15% acetone solution. Figure 3 depicts the desorption kinetic curves for 2,4-D and atrazine. Next, sorption-desorption cycle was carried out

for three cycles of operation. After three cycles (Figures 4 and 5), significant quantity of herbicides could be desorbed and regenerated sorbent could be reused. The sorbent could still be reused till its adsorption capacity was retained at least 50% of that of the original sorbent.

Although solvent regeneration using ethyl alcohol and acetone is the best method to regenerate the rubber granules, it is important to recover these organic solvents to reduce the cost of operation. It was possible to recover the solvents through solvent distillation unit for reuse.

In order to reduce the cost of operation, it is important to recover the organic solvents and to
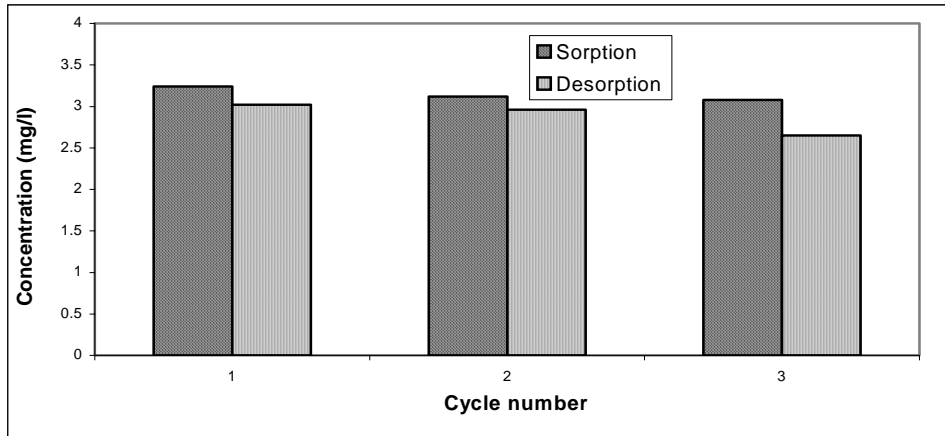
Figure 4.   Regeneration cycle for spent rubber granules by 15% ethyl alcohol solution for 2,4-D
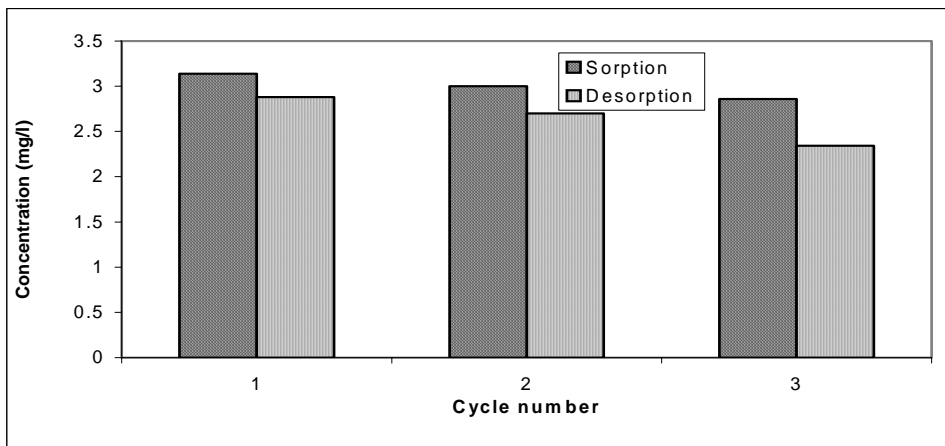

Figure 5.   Regeneration cycle for spent rubber granules by 15% acetone solution for atrazine

reuse them. by solvent extraction method or distillation method, these solvents can be recovered. the reuse of solvent and adsorbent material over many cycles of adsorption and desorption would be ultimately prove to be economical as well as environmentally sound practice for the field application.

COLUMN SORPTION AND DESORPTION

Figures 6 and 7 show the breakthrough curves for 2,4-D and atrazine laced distilled water and tap water. It is apparent from study that 1 g of rubber granules could treat 0.009 l of distilled water or 0.0084 l of tap water spiked with 2 mg l^{-1} of herbicides. The tap water showed an earlier breakthrough when compared to distilled water system, even though the breakthrough curves closely followed each other. The presence of cations (Ca^{+2} and Mg^{+2}) and alkalinity in tap-water were responsible for earlier breakthrough

due to competitive adsorption. In the batch desorption studies,15% ethyl alcohol and 15% acetone were much effective eluents for 2,4-D and atrazine respectively. Hence 15% ethyl alcohol and 15% acetone were used to study the regeneration behavior of waste tyre rubber granules in fixed bed column once the column was completely exhausted. Exhausted columns were left for one day to dry prior to column regeneration studies. Figs. 8 and 9 show the curves for regeneration of spent rubber granules bed for 2,4-D and atrazine, respectively. The amount of adsorption in column was about 4.9 mg and the corresponding desorption by 15% solution was about 4.43 mg for both 2,4-D and atrazine. The regeneration of spent adsorbent bed is essential for efficient and economical use of waste tyre rubber granules. Using the distillation apparatus, the acetone and ethyl alcohol were recovered from 2,4-D and atrazine for reuse. The
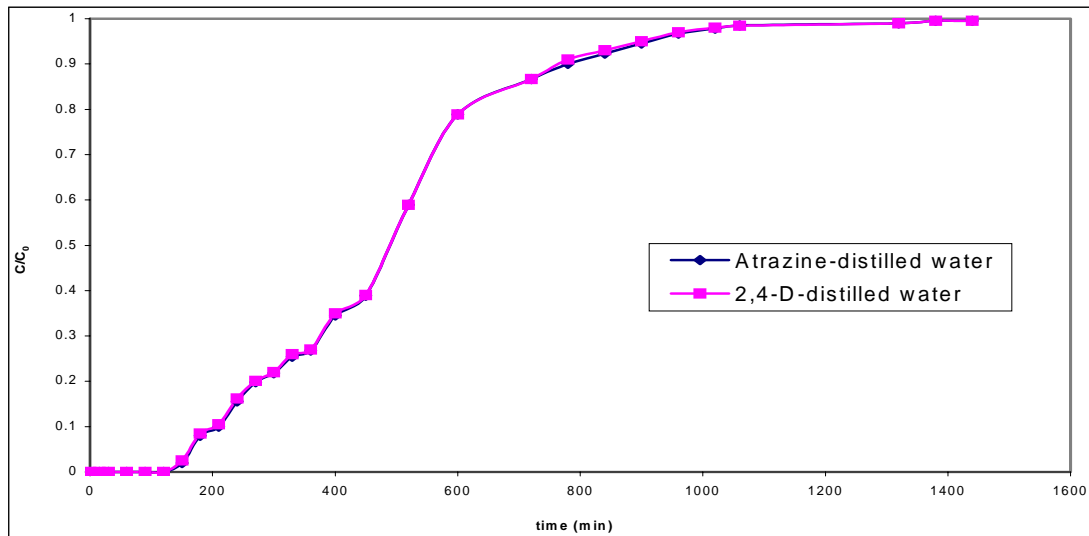
Figure 6. Breakthrough curve for 2,4-D-rubber granules system and atrazine-rubber granules system in distilled water
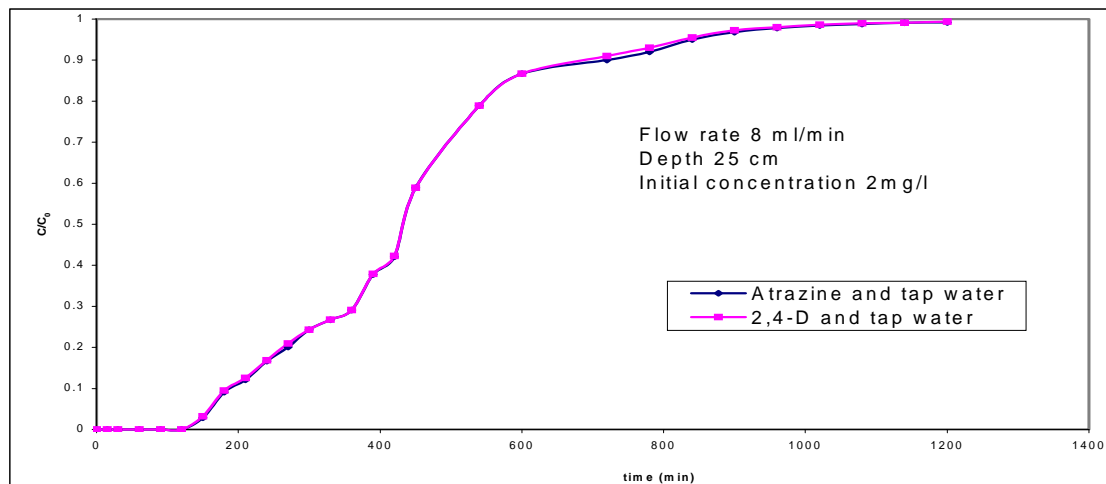

Figure 7. Breakthrough curve for 2,4-D-rubber granules system and atrazine-rubber granules system in tap water

recovery of solvent and its use over many cycles would make the overall process attractive. Once spent adsorbent can be no longer be regenerated to acceptable extent, it will be disposed off properly by following the methods suggested in the next section.

Management of Exhausted Rubber Granules

Disposal of exhausted adsorbents is perhaps the most complex problem. The disposal of spent adsorbent containing hazardous pollutants falls under the hazardous categories and has to be disposed according to according to hazards material regulations. The usual method of sludge management such as thickening, conditioning, de-watering, digestion, incineration and wet oxidation are not applicable to the processing of spent adsorbent. In the case of pesticides and other hazardous compounds, the spent adsorbent is disposed by ultimate disposal methods such as ground disposal, incineration, ocean disposal, chemical degradation and open burning (Dhua, 1989). Ground disposal includes deep wells, sanitary pits, lagoons and surface disposal. In the case of herbicides, this poses a great threat to the environment. Incineration and ocean disposal also cause air pollution and death of useful organisms. Hydrolysis has a significant influence on their existence in parental form. But hydrolytic reactions are slow for the complex
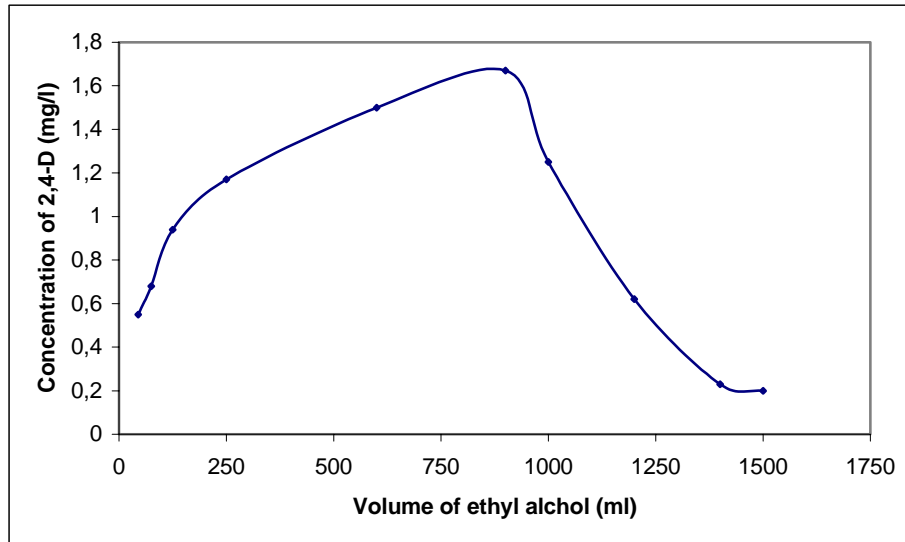
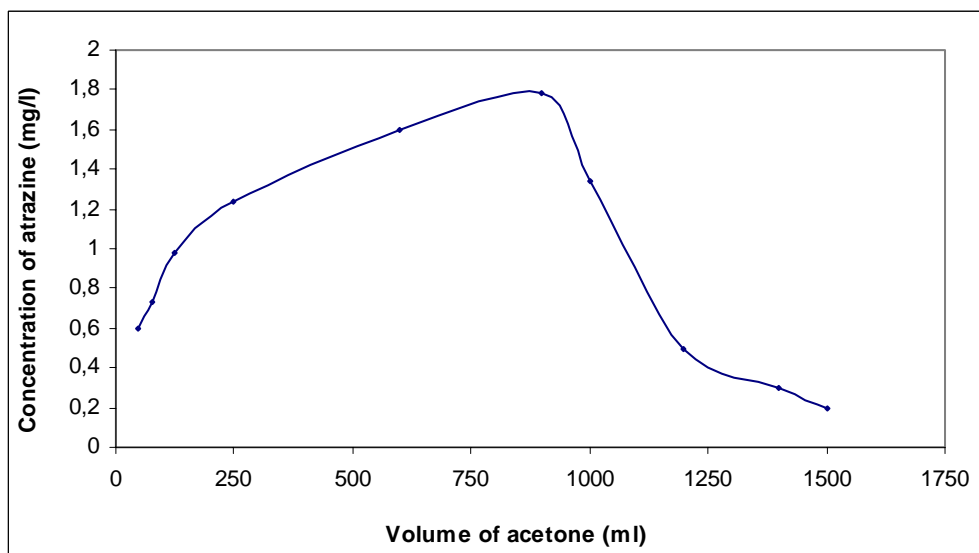*Figure 8.*   Desorption of 2,4-D by ethyl alcohol solution

Figure 9.   Desorption of atrazine by acetone solution

organic compounds (Eichelberger and Lichtenberg, 1971). Moreover the byproducts of these reactions may be more hazardous than parent form. Biodegradation depends on the surrounding environment. Management of exhausted rubber granules is a matter of concern. Improper management or disposal of exhausted rubber granules may create water pollution and soil pollution by leaching. In the present research work, the possibility of the use of exhausted rubber granules as binder of asphalt was investigated as the method for disposing the spent adsorbent. It was found that it is a reasonable method for management of exhausted adsorbent as it not only abates the disposal problem but also helps to reduce the cost of road construction.

The possibility of the use of exhausted rubber granules as an additive to asphalt used for road construction, the mixture of exhausted rubber granules and asphalt was tested for its suitability as road materials as compared to pure asphalt. The percentage of rubber granules was taken as 5%. Indian standard method for testing tar and bitumen (BIS, 1978) has been followed for characterizing specific gravity, viscosity,

penetration and softening point of rubber granules-asphalt mixture. Table 1 shows the comparison between pure rubber granules asphalt mixture and exhausted rubber granules asphalt mixture with the reference to the standard pure asphalt. It is clear from the comparison between the properties of pure rubber granules (5%)-asphalt mix and exhausted rubber granules (5%)-asphalt mix that the decrease of penetration, the decrease of ductility, the increase of specific gravity and the increase of softening point indicated that exhausted rubber granules-asphalt mix was harder than both the pure asphalt-rubber granules mix and pure asphalt (BIS, 1978). The change of viscosity of rubber granules asphalt mix with temperature is shown in Figure 10. This curve was found to be more flat curve than the corresponding curve for pure asphalt with temperature. According to BIS (1974), the flatter curve shows the decreased temperature susceptibility. Thus, the mixture of asphalt and exhausted rubber granules can take higher range of temperature and is less susceptible to temperature. Further, the rubber granules-asphalt mix was kept in the distilled water for a period of 24 hrs to examine the possibility of herbicides existence in the leachates. 2,4-D and atrazine were found to be absent in the leachate. Thus the exhausted rubber granules can be used as admix in asphalt used for road construction without adverse effects.

Table 1. Comparison between pure rubber granules (5%)-asphalt mix and exhausted rubber granules (5%)-asphalt mix [**].

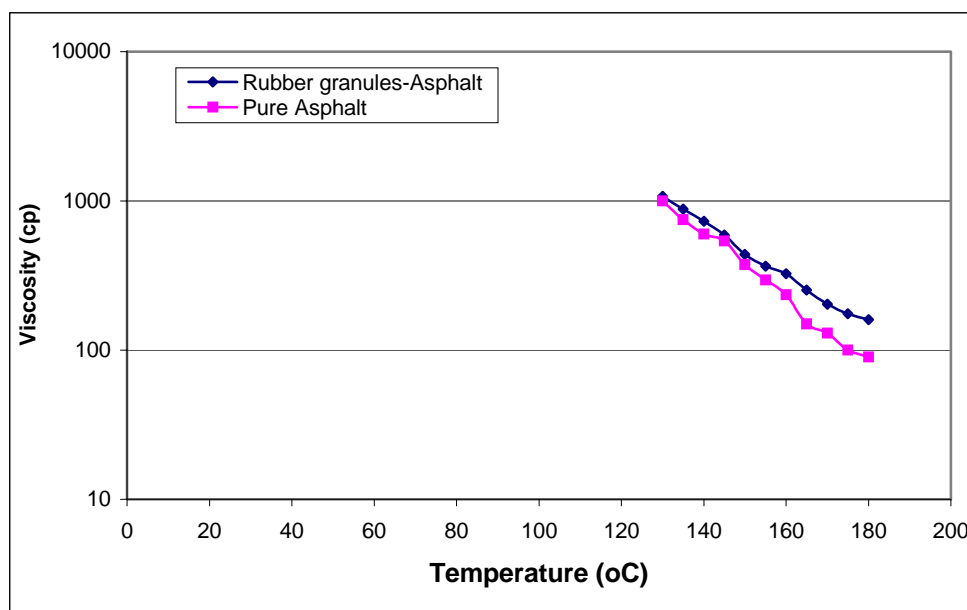| Properties	Pure rubber granules-asphalt mixture	Exhausted rubber granules-asphalt mixture	Pure asphalt
Viscosity at 140^0 C (centi-poise)	700	730	298
Specific gravity	1.029	1.029	1.026
Flash point (^{o}C)	336	331	336
Softening point (^{o}C)	54	55	46
Penetration (mm)	5.8	5.1	9.0
Ductility (cm)	45.5	42	100

[**]based on the average of 10 tests.

Figure 10. Change of viscosity of rubber granules-asphalt system and pure asphalt with temperature

Moreover when rubber granules mixed with hot asphalt, the effects of herbicides will be nullified as the herbicides breakdown at high temperature (Tomlin, 1989). The heating of rubber granules with asphalt will not create additional air pollution because the percentage of rubber is only 5% and heating is done up to 160^0C or less (Collins and Mikols, 1985; King, 1986). Only beyond 180^0C, the thermal separation and smoking of rubber polymer may occur (Hensley, 1998). Still as 2,4-D and atrazine herbicides' vapour pressure is low and their rate of volatilization may be significant, it is suggested that rather than heating the contaminated rubber granules with asphalt, they should be added to asphalt preheated to 160^0C or so. Also, the emissions caused by addition of rubber granules to asphalt were found to be no greater than those by the conventional asphalt. It may concluded from above discussion that after being exhausted, spent rubber granules do not create additional environmental disposal problem when used as binder for asphalt.

CONCLUSIONS

It is evident from the kinetic studies that 83.2% and 87% 2,4-D could be removed by rubber granules in 2 hr corresponding to 0.5 mg l^{-1} and 1 mg l^{-1} initial concentration of 2,4-D in completed mixed batch reactor. The removal was 84.2% and 87.6%, for 0.5 mg l^{-1} and 1 mg l^{-1} atrazine respectively. On the basis of solubility of specific solution and adsorption interaction, 15% ethyl alcohol and 15% acetone solutions were found to be effective solvents for regenerating sorbent containing 2,4-D and atrazine, respectively. Using the distillation apparatus, the acetone and ethyl alcohol were recovered for reuse. This recovery of solvent and its use over many cycles would definitely make the overall process attractive and cost effective. Sorption-desorption study was carried out for three cycles of continuous operation. In general, the removal efficiency was found to decrease after each subsequent cycles for both 2,4-D and atrazine. After three cycles of sorption and regeneration, significant quantity of herbicides could be desorbed and regenerated sorbent could be reused. The sorbent could still be reused over many cycles till its adsorption capacity falls to 50% of that of the original sorbent. Once the sorbent shall be found to be exhausted, it will be used as admix in asphalt used for road construction. Decrease of penetration and ductility and increase of specific gravity and softening point indicated that the mixture of exhausted rubber granules-asphalt was harder than the pure asphalt. Similarly the change of viscosity with time showed that the mixture of asphalt and exhausted rubber granules could take higher temperature and showed decreased temperature susceptibility. Moreover, it did not leach out herbicides or caused emissions more than those by the conventional asphalt. Thus waste tyre rubber granules can be used as an effective and relatively inexpensive adsorbent in water treatment process to remove 2,4-D and atrazine and once exhausted, it can be disposed off by melting it in the asphalt.

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