STUDY AND SIMULATION OF COMPETITIVE SORPTION OF 2,4-D AND PHENOL ON WASTE TYRE RUBBER GRANULES

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ABSTRACT

Batch study for sorption of 2,4-D and phenol on waste tyre rubber granules (WTRG) were carried out for checking feasibility of rubber granules as adsorbent. After 100 minutes of reaction time, it was evident that the kinetics profiles gradually became horizontal indicating the final equilibrium. The removal of 2,4-D and phenol beyond 120 was very low. The removal was 83.2% and 87% in 2hr at 0.75mg/l and 0.4mg/l, respectively for 2,4-D. The removal was 53.2% and 58.7% in 2hr at 0.75 mg/l and 0.4mg/l, respectively for phenol. It is clear from the analysis that Freundlich model fitted well with the experimental data and predicted amount of absorbed well in bi-solute.

Keywords: sorption, phenol, rubber, granules, waste, adsorbent.

INTRODUCTION

2, 4-D and phenol are found in the water bodies. Removal of these compounds is essential because presence of phenolic compounds causes odor. Moreover they are toxic. Many researchers tried to remove these pollutants from water environment. Kannan and Karuppasamy (1998) used tea powder and saw dust as adsorbents for the removal of phenyl acetic acid. They found it as an effective adsorbent with contact time 180min. Singh and Mishra (1990) reported that impregnated saw dust was found efficient adsorbent for removal of phenolic compound. Singh *et al.* (1994) reported that for imprengnated flyash, the maximum removal of phenols was found at a pH 6.5 and a contact time 120min.

The objective of this study was to examine the use of rubber granules as an adsorbent for removal of 2,4-D and phenol for single and bio-solute aqueous solutions. In this work equilibrium adsorption data, effect of pH on the adsorption of phenol and 2,4-D individually and combined from aqueous solutions on rubber granules. Further an attempt is made to evaluate the parameters of isotherms from experimental data on single solute adsorption and the parameters are used to predict the adsorption from bio-solutions assuming ideal conditions.

MATERIALS AND METHODS

Sorbent

The waste tyre rubber granules were provided by Rubber Technology Centre, IIT, Kharagpur, India and sieved to size range 150 -300µm. Rubber granules were washed out distilled water for removal of foreign materials keeping the mixture in plastic bottle at 150rpm in a mechanical shaker for 3hrs. After washing, it was dried for 2 days in sunlight. Then it was oven dried at 50^0-60^0C for 5hrs to remove the moisture present in the pores. It was then cooled to room temperature, sieved to its original size, and stored in airtight bottles.

Characteristics of rubber granules sorbent

Tyres are generally composed of different types of rubber such as textile cords, fabric belts, and vulcanized rubber. Styrene Butadiene Rubber is the widely used polymer by the tyre industries. Carbon black, zinc oxide, natural rubber, sulfur etc. are also added. Carbon black is used to strengthen the rubber (Kim *et al.*, 1997). Bulk specific gravity and porosity of rubber granules were measured using standard methods (APHA-AWWA-WPCF, 1989). The surface area was measured by nitrogen adsorption method (BET 624, Micro-meritics, Germany). Scanning Electron Microscope studies of waste tyre rubber granules were carried out using SEM (LEO S-440, German). It showed the presence of iron compounds, zinc, silica etc. in the rubber granules samples. Zn content was measured by atomic absorption spectrophotometer (AAS 670, Shimazu, Japan). For this Zn was brought to solution form by keeping 2 g Rubber granules in 1:1 HNO_3 solution for 24hrs and after filtration, the filtrate was diluted 25 times for the measurement of Zn. It was found to be 2.3%. The IR spectrum of rubber granules was carried out using IR spectrophotometer (Perkin-Elmer, UK). The peak at 3438cm^{-1} in the IR spectrum indicated the presence of -COOH or -OH group. The peak at 2320cm^{-1} indicated the presence of C≡N, C≡C or C=C or isocyanates group. The other bonding presence in tyre rubber granules were >C=O, C-H bonding and C-O. Thermo Gravimetric Analysis (TGA) was conducted for chemical analysis of waste tyre rubber granules using TGA (DT-40, Shimazu, Japan). The physical and chemical characteristics of waste tyre rubber granules as determined by above tests are described in Table-1 below:

Table-1. Physical and chemical characteristics of waste tyre rubber granules.

Parameters	Values
Bulk specific gravity	0.284 g/cm^3
Porosity	0.12-0.14

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Surface area	0.45-0.78 gm/m^2
Carbon black	48-52%*
Polymer matrix	30-33%*
Other materials	Silica, Zinc oxide, Iron etc.**
Ash content	2-3%

As determined by * TGA test, ** SEM test.
Sourec: Alam, 2002.

Kinetic study

A known concentration of single and bio-solute aqueous mixture of phenol and 2,4-D was prepared by dissolving required amount of solutes. Equilibrium adsorption data were obtained by contacting a known weight of rubber granules (15g/l) with 100ml of solution of required initial concentration in stoppered Erlenmeyer flasks. The flasks were shaken for 3-4hr in a shaker in a thermostatic bath at 25^0C. The samples were filtered through a Whatman No. 5 filter paper to eliminate any fine particles. Then the concentrations were determined by measuring absorbance.

RESULTS AND DISCUSSION

Removal kinetics of herbicides on rubber granules

The removal kinetics of 2,4-D and phenol by the rubber granules for different concentrations are shown in Figure-1. It may be seen that more than 60% of the pollutants were sorbed within 60 minutes 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. The attainment of the equilibrium time for sorption of herbicides or organic pesticides in completely mixed batch reactor (CMBR) was found in the range of few minutes to several hours by many researchers (Aly and Faust, 1965; Tsezos and Wang, 1991). After 100 minutes of reaction time, it was evident that the kinetics profiles gradually became horizontal indicating the final equilibrium. The removal of 2, 4-D and phenol beyond 120 was very low. The removal was 83.2% and 87% in 2hr at 0.75mg/l and 0.4mg/l, respectively for 2,4-D.

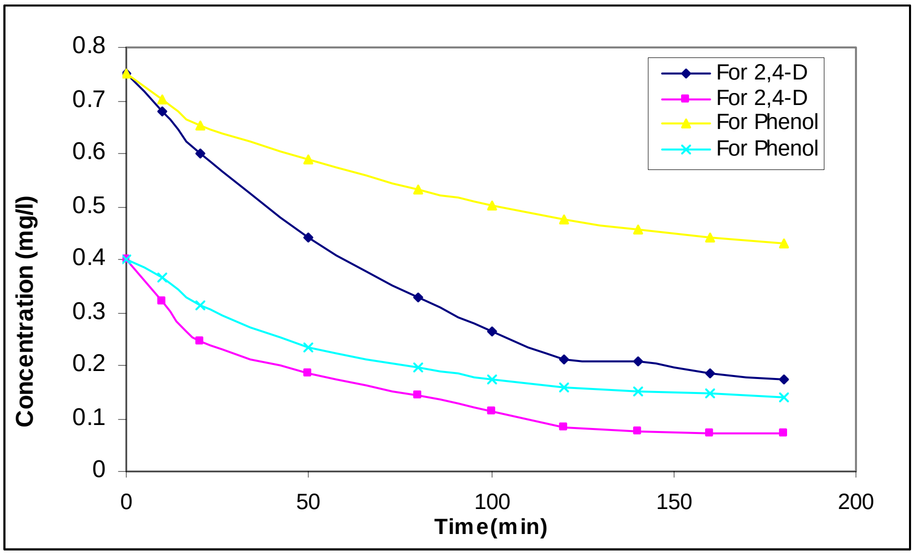

Figure-1. Change of concentration with time for 2,4-D and phenol sorption on rubber granules with initial concentration of 0.75mg/l and 0.4mg/l.

The removal was 53.2% and 58.7% in 2hr at 0.75mg/l and 0.4mg/l, respectively for phenol.

Isotherm study

The equilibrium sorption data of phenol and 2,4-D on rubber granules at 25^0C were obtained and graphically presented in Figure-1. An observation of the results indicates that the amount of solute adsorbed increase with increase in the initial concentration of the solute. Further the extent of adsorption of 2,4-D is more than that of phenol. The bio-solute equilibrium adsorption is presented in Figure-2. From the plot it can be observed that the extent of adsorption of one solute decreases with increase in starting concentration of other solute. But the decrease in the case of phenol adsorption in the presence

2,4-D rubber granules system
Temperature: 27^0C
Size: 0.15-0.30 mm
Dose: 23 gm/l

of 2,4-D than 2,4-D adsorption in the presence of phenol. Further the amount of phenol and 2,4-D adsorbed from bio-solute system is less than the sum of components adsorbed individually at the same concentration. This may be due to competition between the solutes for active site.

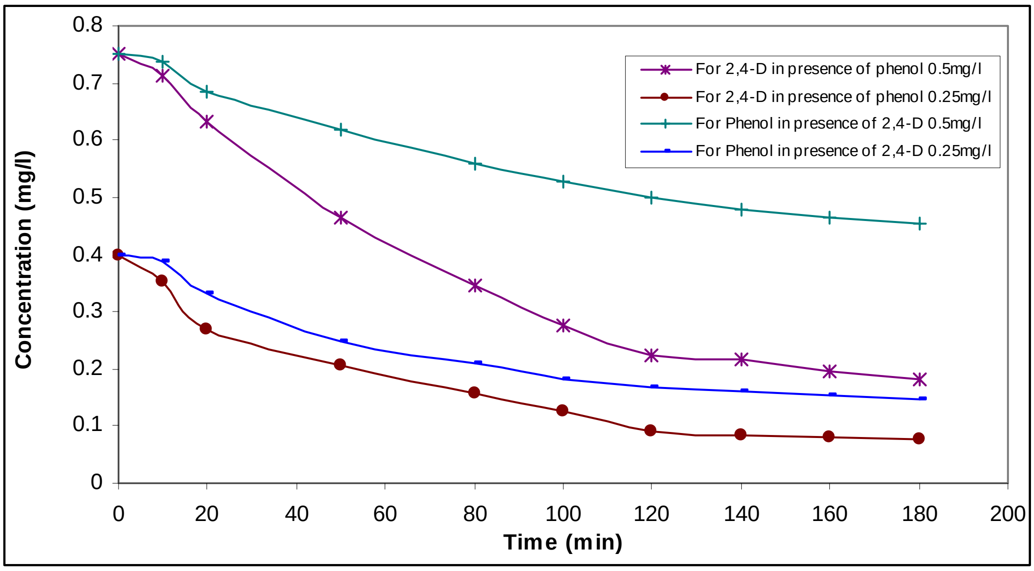

Figure- 2. Competitive sorption of 2,4-D and Phenol in presence of Phenol and 2,4-D, respectively.

For material to be assessed as adsorbent, equilibrium studies have to be conducted. In adsorption process, particular volume or weight of solids is added to the solution containing a certain concentration of pollutant. When the adsorbent comes in contact with the solution, the adsorbate gets accumulated on the surface of the adsorbent. In this process, a dynamic equilibrium would be established which means the migration of adsorbate from solution to the solids get counter balanced by the adsorbate migration from solid to solution. At this position no significant removal of adsorbate is expected further. Equilibrium.-stage at which all potential sites of the adsorbent reach the equilibrium, q_e, the adsorbent is said to be exhausted and the capacity at this point is called maximum adsorptive capacity, Q_{max}. To assess the capacity of any adsorbents saturation adsorptive capacity is the appropriate parameter to be considered. Experimental isotherms are useful for describing sorption capacity to evaluate of the efficacy of an adsorbent. Moreover the isotherm is essential in predictive modeling procedure for analysis and design of sorption systems (Venkobachar, 1990; Das and Bandyopadhyay, 1991). Langmuir model assumes that the sorption energy is constant and independent of surface coverage.

Equilibrium studies were carried out and the experimental isotherm was developed.

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

Screening studies revealed that Langmuir model (Figures 3 and 4) has shown a poor correlation with data followed by Freundlich model (Figures 5 and 6). The equilibrium sorption data of single solutes are fitted to Langmuir ($q_i = a_iC_{i,e}/(1+b_iC_{i,e})$) and Freundlich sorption isotherms ($q_i = ki(Ci_{,e})^{n}{}_{i}$) and the values of the parameters a_i, b_i, k_i and n_i are evaluated using least-square procedure. The parameters are used to predict adsorption from bio-solute solution based on Freundlich and Langmuir multi-solute adsorption models. Tables 2 and 3 show the predicted value of amount of absorbed 2,4-D in presence of phenol with experimental data and predicted value of amount of absorbed phenol in presence of 2,4-D with experimental value, respectively. Figure-7 shows the relationship between predicted values of amount of absorbed 2,4-D in presence of phenol by Freundlich model with experimental data sets. The data sets indicate that the model is capable to represent the results.

$$C_{1,e} = \frac{q_1}{q_1+q_2}\left[\frac{1}{k_1}\left(q_1+\frac{n_1}{n_2}q_2\right)\right]^{\frac{1}{n_1}}$$ ………………..(bi-solute Freundlich model for 2,4-D)

$$C_{2,e} = \frac{q_2}{q_1+q_2}\left[\frac{1}{k_2}\left(\frac{n_2}{n_1}q_1+q_2\right)\right]^{\frac{1}{n_2}}$$ ……………..(bi-solute Freundlich model for phenol)

$$q_1 = \frac{a_1C_{1,e}}{1+(b_1C_{1,e}+b_2C_{2,e})}$$ …………………………(bi-solute Langmuir model for 2,4-D)

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$$q_2 = \frac{a_2 C_{2,e}}{1+(b_1 C_{1,e} + b_2 C_{2,e})}$$ ……………………..... (bi-solute Langmuir model for phenol)

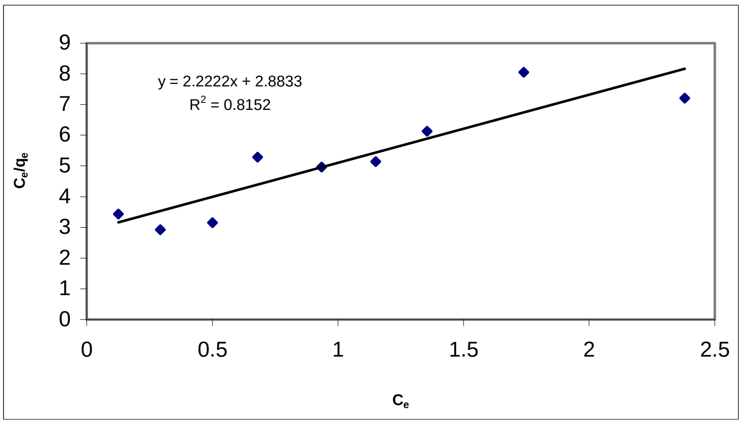

Figure-3. Application of Langmuir model for 2,4-D sorption on waste tyre rubber granules.

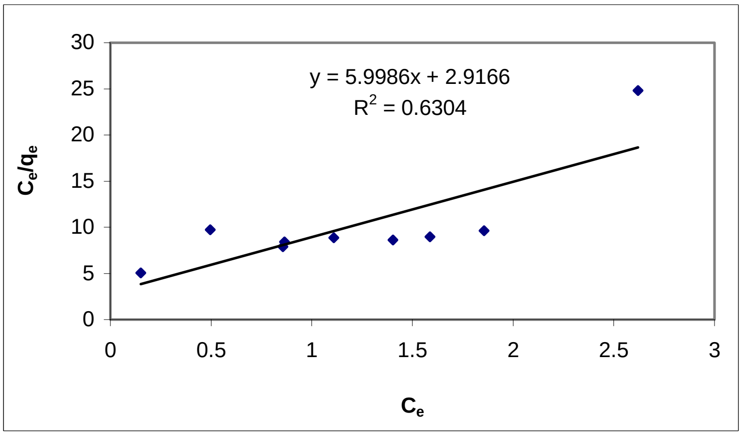

Figure-4. Application of Langmuir model for phenol sorption on waste tyre rubber granules.

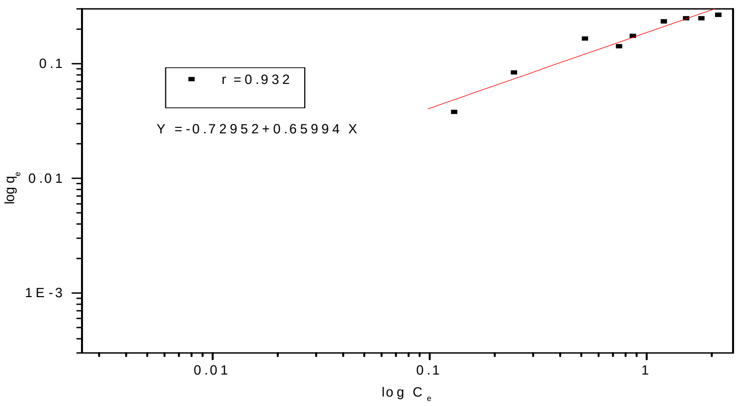

Figure-5. Application of Freundlich model for 2,4-D sorption on waste tyre rubber granules.

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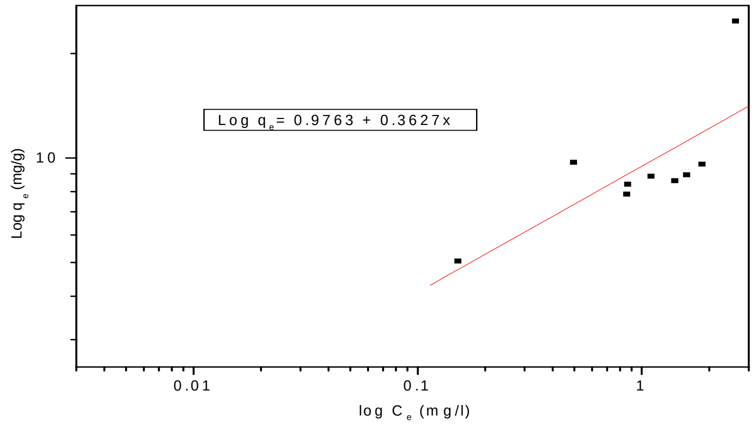

Figure-6. Application of Freundlich model for phenol sorption on waste tyre rubber granules.

Table-2. Predicted value of amount of absorbed 2,4-D in presence of phenol.

Initial concentration of 2,4-D	Phenol concentration	Equilibrium concentration	Predicted absorbed amount of pollutants by Frenundlich	Predicted absorbed amount of pollutants by Langmuir	Experimental absorbed value
0.75	0.75	0.22	0.04167	0.084235	0.0353
0.40	0.75	0.145	0.03124	0.057936	0.0172
0.25	0.75	0.098	0.01434	0.040000	0.0101
0.75	0.50	0.184	0.04135	0.073400	0.03772
0.40	0.50	0.118	0.02134	0.048800	0.01881
0.25	0.50	0.08	0.01234	0.042820	0.01
0.75	0.25	0.148	0.04876	0.059530	0.0401
0.40	0.25	0.088	0.02456	0.037280	0.0208
0.25	0.25	0.06	0.01867	0.025862	0.0127

Table-3. Predicted value of amount of absorbed phenol in presence of 2,4-D

Initial concentration of phenol	2,4-D concentration	Equilibrium concentration	Predicted absorbed amount of pollutants by Frenundlich	Predicted absorbed amount of pollutants by Langmuir	Experimental absorbed value
0.75	0.75	0.6	0.01987	0.1735	0.01
0.40	0.75	0.364	0.02234	0.1114	0.0024
0.25	0.75	0.185	0.02345	0.5909	0.0043
0.75	0.50	0.52	0.01789	0.01537	0.015
0.40	0.50	0.231	0.01786	0.0727	0.011
0.25	0.50	0.160	0.02675	0.5160	0.023
0.75	0.25	0.408	0.01987	0.1240	0.0139
0.40	0.25	0.192	0.01789	0.06146	0.01386
0.25	0.25	0.141	0.00987	0.04591	0.007267

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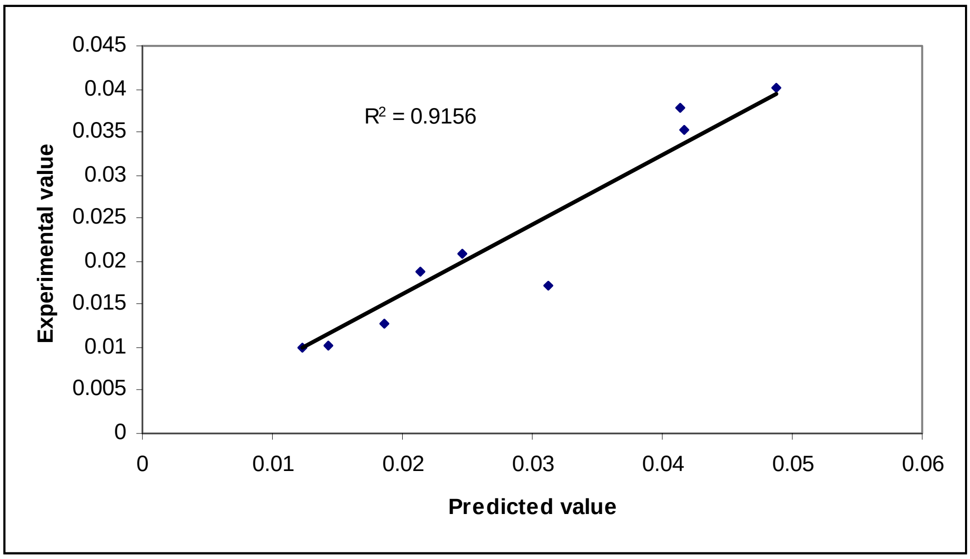

Figure-7. Relationship between predicted q by Freundlich model for 2,4-D in the presence of phenol.

Many researchers (Loganathan, 1977; Venkobachar, 1990 and Alam, 2002) showed that the presence of other pollutants have influence on the sorption of any pollutants. Alam (2002) showed the effect of presence of atrazine on 2,4-D sorption on rubber granules. It was found from his studies that prediction of sorption for bi-solute case is very complex and proper kinetic studies are essential for prediction. Sorption on rubber granules of 2,4-D and phenol may follow the second-degree kinetic reaction rate, so prediction is semi- quantative in nature. Similar result was showed by the study of sorption of 2,4-D and atrazine on rubber granules and heavy metals on waste biomass (Alam, 2002; Osman, 1995).

CONCLUSION

This study was carried out to examine the use of rubber granules as an adsorbent for removal of 2, 4-D and phenol for single and bio-solute aqueous solutions. It was clear from kinetic study that the removal of 2,4-D and phenol beyond 120 was very low. So, 120 minutes was selected as equilibrium time for both the pollutants. The removal was 83.2% and 87% in 2hr at 0.75 mg/l and 0.4mg/l, respectively for 2,4-D. The removal was 53.2% and 58.7% in 2hr at 0.75mg/l and 0.4mg/l, respectively for phenol. The predicted values of q are presented in the result and discussion section with experimental data. The data indicates that both models were capable of reproducing results approximately. Between two models, Freundlich model fitted well with the experimental data and predicted amount of absorbed well in bi-solute. It may be due to better fitting of experimental data with Freundlich model for single solute case.

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