ABSTRACT

Modern agricultural practices often include the extensive use of a wide range of herbicides. Environment contamination due to the extensive and indiscriminate use of these toxic herbicides has become a great concern to the public and to regulatory officials. 2,4-D and atrazine are the two widely used herbicides in the World. It is reported by several researchers that the different components of biosphere is contaminated by these toxic elements. Several treatment methods are available for removing such toxic chemicals from water with varying degree of efficiency, cost and case of operation through each has its own advantages and disadvantages in the application. Depending on the nature of water and wastewater, level of effectiveness and system size, the suitable treatment option can be selected. The present study is directed towards the identification of low cost and environmental friendly adsorbent, which can be adopted in the community level in the developing countries for removal of 2,4-D and atrazine. In the search for alternative adsorbents, which can be used in place of costly activated carbon, waste tyre rubber granules were used. The management of exhausted waste rubber granules was also studied by evaluating its use as the binder of asphalt after being exhausted.

Scanning electron microscope study indicated that rubber granules were porous in nature. Themo Gravimetric Analysis (TGA) and Screening Electron Microscope (SEM) test were conducted to analysis the chemical and physical characteristics of tyre rubber granules. It was clear from these tests that carbon, iron oxide, zinc oxide, carbon black and polymeric matrix were present. Carbon block acted as activated carbon. The waste tyre rubber granules were used to remove the herbicides 2,4-D and atrazine from aqueous solution. The investigations were carried out in three stages-batch sorption studies, batch desorption and regeneration studies and fixed bed studies.

In the batch studies, kinetic study was conducted in order to find out the order of degree of kinetic equation for sorption of 2,4-D and atrazine onto waste tyre rubber granules. It was found that the sorption of both 2,4-D and atrazine onto waste tyre rubber granules was found rapid and the reaction followed 2^{nd} order kinetics. The second order kinetic equation gave higher regression coefficients than those obtained from 1^{st} order kinetic equation at higher concentrations. At low initial concentrations, the 1^{st} order kinetic equation gave better regression coefficients. Apart from kinetic and isotherm studies, the effects of different parameters such as pH, adsorption dose, adsorption size, presence of chloride, calcium and magnesium were studied. All the parameters were varied one at a time to study their effect on the adsorption process.

The rate limiting step was determined by kinetic data, by the effect of initial adsorbate concentration and adsorbent size on the removal rate and by the interruption test. Mass transformation mechanism was studied with the help SPNSM model. It was found from the model that both external mass transfer and intra-particle mass transfer played important role.

It was found that waste tyre rubber granules could be effectively used as media for the removal of 2,4-D and atrazine from water. Removals were found 78% for 2,4-D and 82% for atrazine with initial concentration of 4 mg/l and dose of adsorbent 18 g/l respectively. Tyre rubber granules could be used for the selective removal of the herbicides from water environment up to certain extent over other ions such as Cl^{-1}, Ca^{+2} and Mg^{+2}.

The equilibrium adsorption data fitted to Langmuir, Freundlich, BET and L-G models. But experimental data was fitted well with BET and Freundlich models. The maximum adsorption capacity was found to be 0.4 mg/g for 2,4-D and 0.47 mg/g for atrazine. The removal of both 2,4-D and atrazine by tyre rubber granules was pH dependent. For case of 2,4-D, pH was kept with range of 5~5.5 whereas pH 5.5~6 for atrazine. Removal efficiency decreased with presence of butachlor, but the presence of chloride, magnesium and calcium ions did not affect the removal significantly. The presence of fertilizer urea and SSP (up to 20 mg/l) also did not affect the removal efficiency significantly. Spent adsorbent could be regenerated with 15% ethyl alcohol for 2,4-D and 15% acetone solution for atrazine. The regeneration study was conducted for 3 cycles.

Fixed bed reactor (FBR) studies were conducted to determine the breakthrough and exhaustion point of waste tyre rubber granules in a perplex column of 3 cm internal diameter at upflow rate of 4 ml/min and 8 ml/min. 12.5 cm, 25 cm and 40 cm bed depths with adsorbent size 150-300 μm were tried and corresponding breakthrough curves were developed for initial concentration of 2 mg/l 2,4-D and atrazine separately. Turbidity was found to have a negative effect on removal efficiency of adsorption process due to blocking the pore of adsorbent. It was found that the removal efficiency decreased about 16.2-18.5 % at 30 NTU. It was also found that pH range of 4 to 6 was suitable for column studies. The tests were conducted with synthetic herbicide samples in both distilled and tap water and it was found that 1gm of rubber granules could treat 0.0212 l of distilled water or 0.0183 l of tap water spiked with 2 mg/l of herbicides. The tap water showed an early breakthrough as compared to distilled water system. The presence of cations (Ca^{++} and Mg^{+2}) and alkalinity in tap water was responsible for early breakthrough. Theoretical breakthrough curves for 2,4-D and atrazine were constructed for 8 ml/min flow rate and 40 cm depth on the basis of BET isothermal studies using the method proposed by Michaels (1952) and were compared with experimental breakthrough curves. Both the curves revealed a better correlation for both 2,4-D-rubber granules system and

atrazine-rubber granules system. Thus BET isotherm model can be used for the prediction of the breakthrough in FBR. The break points for initial concentration of 1 mg/l and 2 mg/l were found 687 min and 420 min respectively for bed depth 40 cm. For the bed depth of 25 cm, the effect of flow rate was analyzed. It was found that for flow rate 8 ml/min and 4 ml/min, the break points differed by about 550 min.

Bed depth-service time (BDST) approach was adopted to find out sorption capacity, service time, sorption velocity, critical bed depth, total capacity and efficiency of the bed etc. using the breakthrough results for three different bed depths of 12.5 cm, 25 cm and 40 cm. The fractional capacity was found to be 0.40277 from the computer program developed on the basis of Ong's work. Depth of adsorption zone was found approximately 36.85 cm for 2,4-D-rubber granules system and 37.45 cm for atrazine-rubber granules system respectively.

Fixed bed desorption and regeneration studies were conducted to investigate the possibility of reuse of spent adsorbent. Organic solvents 15% ethyl alcohol and 15% acetone solution were used for regeneration at 5 ml/min.

In the fourth and final phase, the studies on management and disposal of exhausted adsorbents were also carried out. The possibility of using exhausted rubber granules as binder of asphalt was evaluated in details. The comparison between pure rubber granules (5%)-asphalt and exhausted rubber granules (5%)-asphalt mixture on the properties of asphalt was conducted. The decrease of penetration, decrease of ductility, increase of specific gravity and increase softening point of the mixture of exhausted rubber granules-asphalt indicated that the mixture of exhausted rubber granules-asphalt was harder than the pure asphalt or mixture of rubber granules-asphalt. Also the trend of the change of viscosity with temperature indicated that the mixture of exhausted rubber granules-asphalt can take higher temperature and showed increased temperature susptibility. Due to heating of rubber granules with asphalt, the effects of herbicides were expected to be nullified. The use of rubber will also reduce the noise pollution and the cost of road construction.