Removal of Acetaminophen from Aqueous Systems

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ABSTRACT

The study focuses on the removal of the pharmaceutical drug acetaminophen from aqueous systems. A comparison of physical and biological method of removal was done using column studies. Physical adsorption was performed using aquifer material and biodegradation was done through biofilm developed on pumice stone. Batch studies were also performed to determine adsorption constants. The batch studies showed that adsorption followed Freundlich isotherm. However comparison of physical and biological methods showed biodegradation as a better method for removal of acetaminophen from aqueous systems.

Keywords: acetaminophen, adsorption, isotherm, biodegradation

1. INTRODUCTION

Acetaminophen is one of the most commonly used pharmaceutical drugs worldwide to reduce temperature and pain. It is used in many brands of non-prescription medications. It is often combined with other drugs in some prescription pain medications. There are two main sources of acetaminophen to the environment. When acetaminophen is consumed, about 30 percent of it passes out of the body (unchanged) in urine.

This means it gets flushed down the toilet and mixes with wastewater. Other sources of acetaminophen to wastewater are people disposing off excess or expired medication in the sink or toilet as well as untreated wastewater from treatment plants or manufacturing units .Acetaminophen is generally found in wastewaters at a concentration of about 30-40 µg/L[1]. It has also been detected at high concentrations of 400µg/L on water from pharmaceutical industries and hospital wastewaters.[2] The objective of this report is to compare physical and biological methods for removal of acetaminophen from aqueous systems.

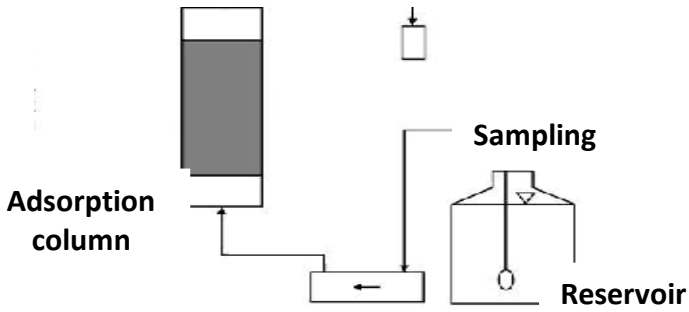
2. MATERIALS

The acetaminophen was obtained from Sigma-Aldrich. Solutions were made in tap water. The aquifer material for adsorption study was taken from Srinagar. UV-A (ultra violet absorption at λmax) was measured using HACH model DR-5000. The pumice stone for biodegradation studies was enriched with activated sludge from the sewage treatment plant in Haridwar.

3. METHODOLOGY 1: ADSORPTION

Batch studies: All adsorption experiments were carried out on a mechanical shaker at 200 rpm using 300 mL conical flasks. A series of experiments were carried out at room temperature (25°C). The first experiment was to study the isotherm for different acetaminophen concentration. 100 mL of solutions with different initial concentrations of 50, 100, 200 and 300 ppb were prepared. Then, the solution and 0.2 g of aquifer material was added into the flasks and then horizontally shaken for 1 hour at 200 rpm and then centrifuged at 30,000 rpm for 1 hr. The supernatant was measured absorbance by using UV-spectrophotometer at λmax equal to 291nm [3, 5].

Continuous experiment: Columns packed with aquifer material from Srinagar were used for continuous experiment. The parameters of the soil column used in the experiments are given along with Fig 1 .A tap water solution containing the substance of interest ie. acetaminophen was continuously fed through a fixed-bed column. Samples were taken from the column outlet and the measured concentration was plotted versus time to get a breakthrough curve.[4]

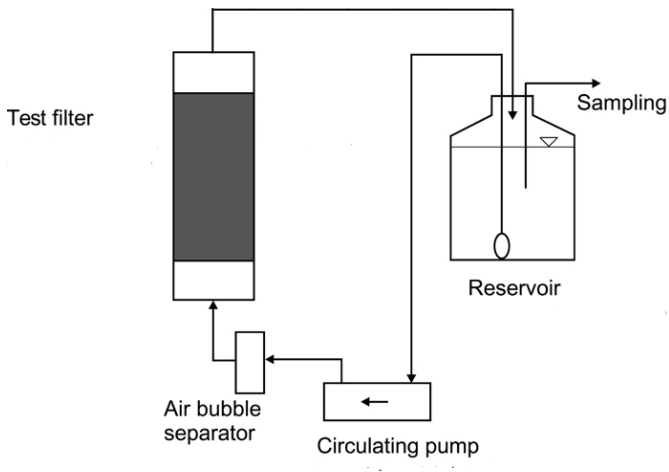


- Volume of column = 727 cm^3
- Mass of soil= 4 kg
- Flow rate= 2ml/min
- Detention time= 2.6 hours

Fig 1: Experimental setup for adsorption analysis

Methodology 2: Biodegradation

Experiment: Biological degradation of acetaminophen was studied in the laboratory using a biologically active test filter. Fig. 2 shows a typical test filter set-up. The filter column was filled with an inert solid material. In this experiment, the material used was pumice stone[4,6]. The details of the column are given in Fig2. As a first step, the filter was conditioned with activated sludge for 2 weeks having high BOD. It was then conditioned with fresh river water from the Ganges. This water was percolated through the fixed bed for about one week to form a biofilm of typical microorganism populations. After conditioning, the reservoir bottle was filled with a solution of tap water containing the test compound. The spiked river water was percolated through the filter material. Biological degradation takes place in the biofilm and the decrease in concentration was determined by taking samples from the reservoir after defined time intervals.[6]



- Volume of column = 727 cm^3
- Mass of pumice stone = 3.2 kg
- Flow rate= 2ml/min
- Detention time= 2.2 hours
- Porosity=56%

Fig 2: Experimental setup for biodegradation analysis

4. RESULTS AND DISCUSSIONS

Sieve analysis: From sieve analysis the effective size D_{10} was estimated to be 0.04 mm. It can be seen that the aquifer material has a high percentage of fines.

Adsorption curve: From the column study an adsorption curve was plotted. The adsorption curve gives the time taken for the column to achieve different percentage of breakthrough. 100% breakthrough was obtained in a time period of about 54 hours

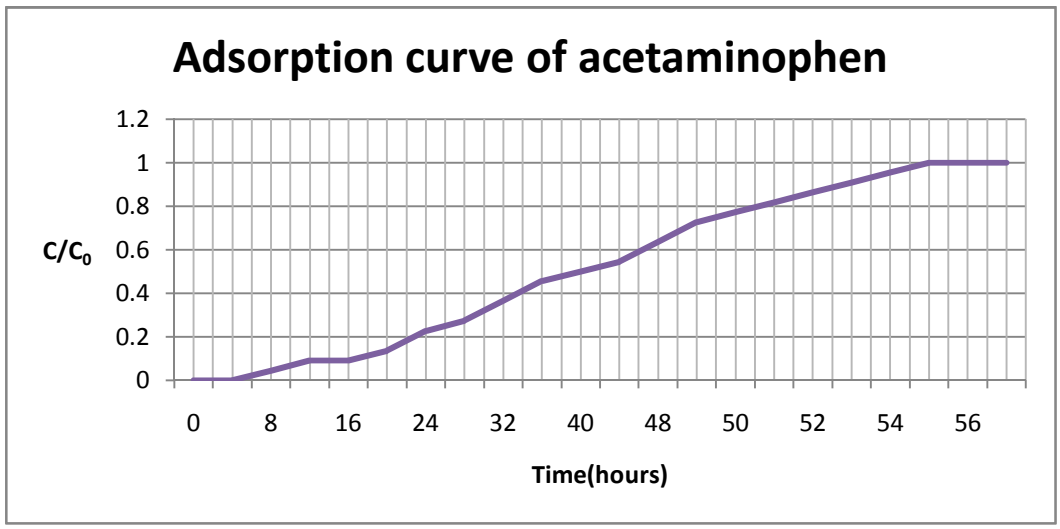


Fig3: Graph showing adsorption curve of column study.

Isotherm studies: Data obtained from batch studies was found to be in conformity with *Langmuir* and *Freundlich* isotherms. Langmuir isotherm was obtained using the linearised equation $(C_e/q_e) = (1/bq_m) + (C_e/q_m)$ and Freundlich isotherm was obtained using $(\log q_e) = (\log k_f) + (1/n \log C_e)$ [5]

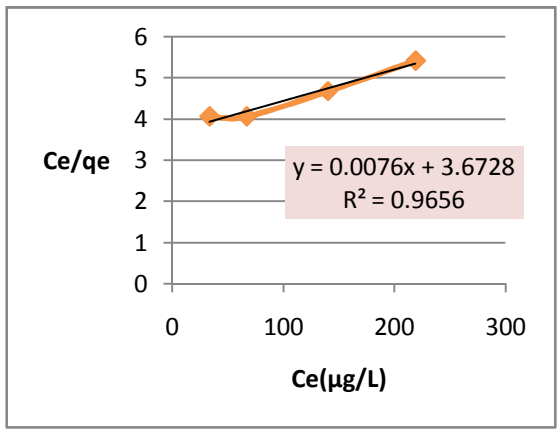


Fig 4:Lamgmuir isotherm

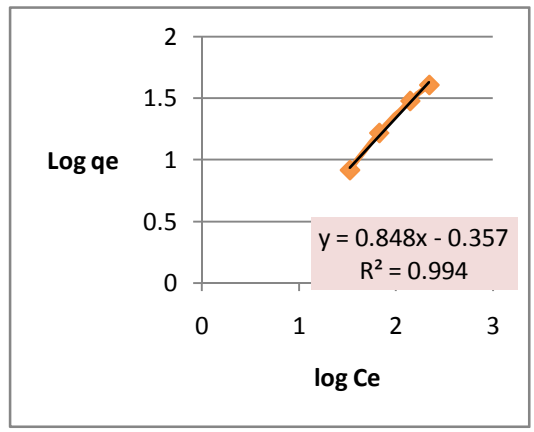


Fig 5: Freundlich isotherm

Batch	Langmuir isotherm	Freundlich isotherm
Batch 1	R^2=0.9656	R^2=0.994

Table 1 : Comparison of R^2 values of the batch studies for Langmuir and Freundlich isotherms

The observations indicate that the aquifer material follows Freundlich isotherm

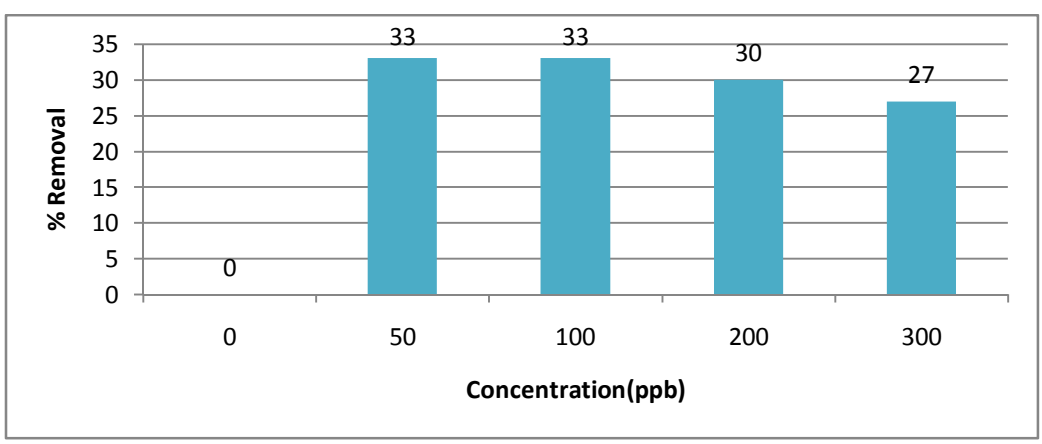


Fig 6: % removal for different concentrations of acetaminophen

5. BIODEGRADATION CURVE

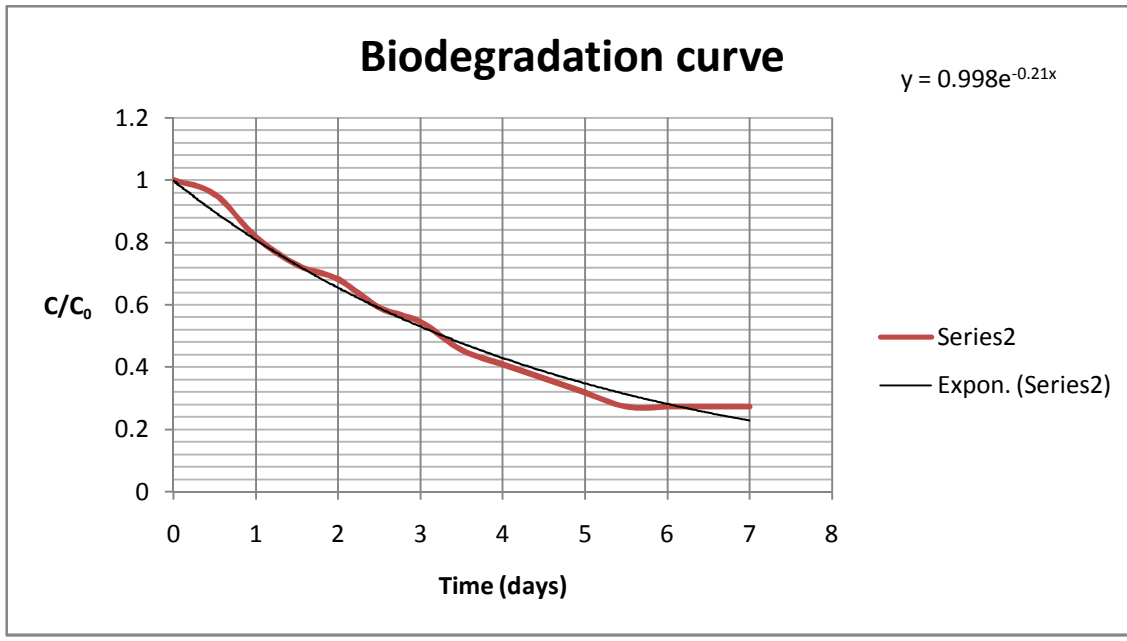


Fig 7: Degradation curve for biodegradation analysis

- Degradation rate constant = 0.211 d^{-1}
- $t_{1/2}$= 3 days

6. CONCLUSION

The adsorption studies of the column indicate that acetaminophen isn't effectively removed by adsorption. This could be attributed to the highly hydrophilic nature of the compound having a log Kow value of 0.46[7].Both batch studies indicate that the soil fits the Freundlich isotherm more appropriately indicating a heterogeneous adsorption. The percentage removal graphs show no major increase with the change in concentration of the feed solution or with change in dose of adsorbent. Biodegradation showed a removal of about 73% in about 5.5 days. Hence it can be clearly concluded that biodegradation is a better method of removal of acetaminophen from aqueous systems as compared to adsorption. Further studies can be done using advanced oxidation processes like ozonation and using Fenton's reagent to study the removal by chemical methods.

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