# PERFORMANCES OF LOW – COST REACTIVE MATERIALS AS PERMEABLE REACTIVE BARRIER MEDIA TO TREAT LANDFILL – LEACHATE

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#### Abstract

The landfill-leachate is deemed to be one of the most serious pollution problems because landfill- leachate- polluted ground water riches in various hazardous contaminants. Permeable reactive barriers (PRBs) are considered a low cost and effective alternative for remediating contaminated sites. The availability and the cost are important criteria in selecting a reactive material. Therefore in this study a laboratory scale column experiment was conducted to study the feasibility of a PRB with low cost-locally available reactive materials such as coconut coir fibre, rice straw, saw chips and rice husks to remedy the landfill- leachate. The leachate was collected from the Galle-municipal-council dumpsite. The column experimental set-up consisted of 4 columns each with 35 cm height and 8.9 cm diameter. The initial length of the reactive media was 26 cm in each column. The influent which was stored in an overhead tank was loaded on to the column via a shower. An application rate of approximately 0.4 mL/s was maintained by adjusting a valve. The effluent was collected in an effluent tank kept below each column. Influent and effluent were characterized in terms of several wastewater parameters. Each reactive material was mixed with laterite soil so that soil to reactive material ratio became 2:1 on weight. Adsorption and biological uptake could be the dominant treatment mechanisms of organic matter. Rice straw and saw chips reduced COD concentration to greater than 80 percent within two days of application. In considering the overall removal of organic matter, saw chips were the best at both adsorption and biodegradation; coconut coir fibre and rice husks were the best at biodegradation; both rice straw and saw chips were equally good at adsorption. Ammonia could be treated mainly by adsorption and nitrification. Based on the results, rice husks could be the most supportive reactive media for nitrification. Though there were enough carbon sources and anaerobic zones, denitrification was not significant. Adsorption could be the dominant mechanism for chloride removal in all media that equally performed in removing chloride with greater than 90 percent removal.

Keywords: PRB, Leachate, Reactive media, Column tests, Organic materials

# 1. Introduction

A great deal of money and effort has been spent on environmental restoration during the past several decades. Significant progress has been made improving air quality, cleaning up and preventing leaching from dumps and landfills, and improving surface water quality, although significant challenges still exist in all of these areas. Among the more difficult and expensive environmental problems, and often the primary factor limiting closure of contaminated sites following surface restoration, is contaminated ground water. It is well accepted that landfills which take biodegradable waste such as municipal solid waste pose a hazard to the environment including ground water, surface water and soil. It is for this reason that controls are needed at such sites. The landfill - leachate is deemed to be one of the most serious pollution problems because landfill- leachate- polluted ground water riches in various hazardous contaminants.

The most common technology used for remediating ground water is surface treatment where the water is pumped to the surface, treated and pumped back into the ground or released at a nearby river or lake. It has proved singularly unsuccessful for a number of potentially harmful chemicals, for example heavy metals leaching slowly from contamination sources, PAH with low bio- availability, etc.Costs of this type of remediation are often very large. Although traditional pump-and-treat technologies are still useful for certain remedial scenarios, the limitations of them have recently been recognized, along with the need for innovative solutions to ground water contamination {Keely (1989), National Research Council (1994)}.

Permeable reactive barrier (PRB) which is an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provides a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals down gradient of barrier (USEPA 1998). They are considered a low cost, effective alternative for remediating contaminated sites. The technology of PRBs could potentially allow many more contaminated sites to be remediated effectively, thus greatly enhancing natural groundwater protection. Groundwater remediation using PRBs is an in situ method with low energy demand and therefore more cost-effective than standard remediation techniques (Manz et.al., 1997). It is a passive, in situ technology that has a high potential to treat shallow aquifers at a lower cost than traditional pump-and-treat methods, but due to a lack of long-term data, its cost-effectiveness has not been proven {Naftz et al. (2002), Roehl et al. (2005)}. However, Schad and Gratwohl (1998) found that the remediation costs can be up to 50 percent less than pump-and-treat methods based on data collected at several sites. In addition, using PRBs reduces contaminant exposure to humans and allows the overlying land to be actively used during remediation. A wide variety of pollutants are degraded, precipitated, sorbed or exchanged in the reactive zone, including chlorinated solvents, heavy metals, radio nuclides and other organic and inorganic species {Puls et al. (1999), USEPA (1997)}. Therefore making PRBs cost-effective is imperative. In order to achieve this, experiments on low-cost reactive media is of utmost importance.

The main engineering challenge is determination of suitable type and amounts of reactive materials in a permeable wall and proper placement techniques. The availability and the cost

are important criteria in selecting a reactive material. Continuing controlled column experiments for prolonged periods of time provides an opportunity to derive the treatment system (Blowes et al., 1997). Therefore the aim of this study was to conduct laboratory scale investigations on low-cost, locally and readily available materials such as coconut coir fibre, rice straw, rice husks and saw chips to be used as a reactive material in a PRB wall to treat effectively the landfill leachate.

# 2. Methodology

Laboratory-scale column tests were conducted to determine basically the treatment efficiency of biodegradable organic matter, nitrogenous compounds and chlorides. Figure 1 shows the experimental set-up.



Figure 1: Experimental setup

It consisted of 4 columns each with 35 cm height and 8.9 cm diameter. At the bottom of the column initially existed a 7 cm thick gravel layer. The initial media height was 26 cm. There was a perforated plate between the media and the gravel layer to distribute effluent evenly to the gravel layer. There was another perforated plate over the media at the top of the column to distribute influent evenly throughout the column and to prevent by-passing of water. The influent which was stored in an overhead tank was loaded on to the column via a shower. An application rate of approximately 0.4 ml/s was maintained by adjusting a valve. The effluent was collected in an effluent tank kept below each column. The influent was the leachate collected from the dumpsite of Galle municipal council. Two series of column experiments were conducted with reactive materials coconut coir fibre, rice straw, rice husks and saw chips. All the reactive materials were washed and then dried before loading. Rice straw was cut into about 2 cm pieces. Each reactive material was mixed with laterite soil so that soil to reactive material ratio became 2:1 on weight. The compaction density of reactive material was kept

constant. Influent and effluent were characterized in terms of several wastewater parameters such as biochemical oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD), nitrate – nitrogen, ammonia-nitrogen, total nitrogen and chloride. All the analyses of wastewater were in accordance with the Standard Methods for the Examination of Water and Wastewater (1998). Table 1 shows the influent characteristics. The duration of each experimental run was 9 days.

Parameter	Series 1	Series 2
COD (mg/L)	48 000	8 492.3
$BOD_5(mg/L)$	25 300	243
Ammonia Nitrogen (mg/L)	834	341.9
$NO_3^{2-}N(mg/L)$	228	134.5
Cl(mg/L)	10 497	8997

Table 1: Concentration of different parameters in influent

### 3. Results and Discussion

### 3.1 Introduction

The following sub sections show how organic materials, nitrogenous compounds and chlorides were removed by laboratory-scale columns with reactive media. Since unsaturated conditions prevailed in all four columns, the treatment mechanism was expected to be greatly similar to natural attenuation in the unsaturated zone of soil. Bagchi (2004) identified following mechanisms of leachate attenuation in soil: adsorption, biological uptake, cation-and anion-exchange reactions, dilution, filtration and precipitation. However these columns differed from the unsaturated zone due to the presence of reactive media which were organic materials. Reactive media also altered the natural pore structure of the undisturbed soil. It was expected that these conditions would improve the attenuation of some parameters like organic matter, nitrogenous compounds and chlorides. The columns were opened at the top. Therefore at the upper layers, aerobic biodegradation was possible and at the middle and bottom layers both aerobic and anaerobic conditions could exist.

#### 3.2 Removal of organic materials

The fate of organic matter in the columns was determined by measuring COD and  $BOD_5$  concentrations in the effluent. Both COD and  $BOD_5$  were reduced while flowing through columns. Bagghi (2004) stated that the most important mechanism of COD attenuation in soil is biological uptake, and filtration is a minor mechanism. According to the same author, the surfaces of organic matter provide some adsorption sites; in addition they may serve as energy source for microorganisms. Activated carbon is used to remove a portion of the remaining

dissolved organic matter after secondary treatments (Metcalf and Eddy, 2003). Therefore adsorption can also be considered a potential removal mechanism of organic materials in the columns with organic reactive media. Figure 2 shows the variation of percentage removal of COD with time for the four different types of reactive media. The removal percentage in the experimental run 1 was more than 70 % throughout the entire period. The removal percentage remained almost constant in rice straw and saw chips which reduced the COD to more than 80 % within two days of application. According to run 1, rice straw reduced the highest amount within the shortest time period while rice husks removed the highest amount of COD within the entire experimental run. Since the reactive materials in all four columns were organic materials, adsorption may have taken place in all columns. The removal percentage in experimental run 2 in most occasions lied below those of run 1. It took 9 days for run 2-removal rates to reach the figures of 1<sup>st</sup> run. Unlike the run 1, the removal percentage gradually increased with time in the run 2. Therefore adsorption could be the dominant treatment mechanism in run 1, and the principal treatment mechanism in run 2 could be biological uptake. Sorption refers to the exchange of molecules and ions between the solid phase and the liquid phase (Metcalf and Eddy, 2003). Hence vacant sites for adsorption decrease with time leading to lesser sites for adsorption to take place. Biodegradation takes some time to execute because it needs the synthesis of microorganisms.



Figure 2: Percentage removal of COD with time (CCF-Coconut coir fibre; RS-Rice straw; SC-Saw chips; RH-Rice husks; 1-Experimental series 1; 2-Experimental series 2)



Figure 3: Percentage removal of BOD<sub>5</sub> with time (CCF-Coconut coir fibre; RS-Rice straw; SC-Saw chips; RH-Rice husks; 1-Experimental series 1; 2-Experimental series 2)

Figure 3 shows the variation of percentage removal of BOD<sub>5</sub>. There is no clear difference between the results of run 1 and 2 as of COD. It implies that the dominant treatment mechanism of biodegradable portion of organic matter could be biological uptake. In fact the fact that percentage removal increased with time confirms that the major mechanism of removal could be biodegradation since the rate of removal by adsorption is rapid at the beginning and decreases with time. Though coconut coir fibre being the least performer in COD removal, it was very good at removing BOD<sub>5</sub>. Both coconut coir fibre and saw chips performed the best in overall BOD<sub>5</sub> removal in both runs. Though rice husks showed poor performances at the very beginning, the percentage BOD<sub>5</sub> removal increased rapidly with time.Therfore it can be suggested that rice husks is good at biodegradation rather than adsorption.

Overall saw chips were the best at both adsorption and biodegradation. Coconut coir fibre and rice husks were the best at biodegradation. Both rice straw and saw chips were equally good at adsorption.

#### 3.3 Removal of nitrogenous compounds

Figure 4 shows the percentage removal of ammonia-nitrogen by each column. The highest removal rate in the experimental run 1 occured on the 2<sup>nd</sup> day. It indicates that the adsorption could be dominant in run 1. Cation exchange could also be possible, however the media lacked cations because percent soil amount was less in each column. In the experimental run 2, higher percentage removals could be seen on the last day of experimental run. It implies that the biological uptake could be dominant in run 2. The columns represented attached growth systems with regard to microbial degradation. In attached growth systems used for nitrification, most of the  $BOD_5$  must be removed before nitrifying organisms can be established. The heterotrophic bacteria have a higher biomass yield and thus can dominate the surface area of fixed-film systems over nitrifying bacteria. Nitrification is accomplished in an attached growth reactor after BOD<sub>5</sub> removal or in a separate attached growth system designed specifically for nitrification. (Metcalf and Eddy 2003). Therefore nitrifiers may have been synthesized with time and increased the nitrification rate. In both runs, rice straw showed overall high percentage removal with the 9<sup>th</sup> day of run 2 exceeding 90%. Overall performance of coconut coir fibre in run 2 was low compared to other media. As in the case of organic matter, the removal rate in rice husks in both runs increased at later times. According to results of run 1, saw chips also performed well.

Figure 5 shows the variation of nitrate – nitrogen concentration with time. Figure 6 shows the percentage removal of total nitrogen with time. In run 1, there was no much variation in nitratenitrogen concentration when compared with that in the influent. However, nitrate-nitrogen concentration in run 2 increased rapidly with time. This is an indication that nitrification executed in all the columns. According to Bagghi (2004), the major attenuation mechanism of nitrate is biological uptake. These results are comparable with the results of ammonia. As mentioned above, adsorption could be dominant in run1, hence there was no addition to nitrate-nitrogen concentration. In run 2, there was more nitrification, hence nitrate-nitrogen concentration increased. Rice husks gave the highest concentration of effluent-nitrate throughout the experimental run 2. Therefore rice husks can be considered as the most supportive reactive material for nitrification. The biological denitrification or reduction to gaseous nitrogen or nitros oxide requires anaerobic conditions and a carbon source (Bagghi, 2004). Though there was enough carbon sources and anaerobic zones, the increase of nitrate concentrations indicates that denitrification was not significant.



*Figure 4: Percentage removal of NH*<sub>3</sub>-*N with time(CCF-Coconut coir fibre;RS-Rice straw;SC-Saw chips;RH-Rice husks;1-Experimental series 1;2-Experimental series 2)* 



Figure 5: Concentration of  $NO_3^{2^2}$ -N in effluent with time(CCF-Coconut coir fibre;RS-Rice straw;SC-Saw chips;RH-Rice husks;1-Experimental series 1;2-Experimental series 2)

### 3.4 Removal of chlorides

Figure 6 shows the percentage removal of chloride with time. It is notable that removal percentage in all reactive media was higher than 80 % in experimental run 1, however the removal rate decreased below 40 % in run 2. This indicates that reactivity of the media had greatly lost in run 2. It hints that the reaction mechanism may have been either ion exchange or adsorption of which the removal rate is proportional to the vacant sites. Chloride is not attenuated by any soil type and is highly mobile under all conditions (Gerhardt 1977). Dilution is the only mechanism for of attenuation of chloride in soil (Bagghi, 2004). However the

opposite of above statements happened in these columns because they had organic matter that increased the adsorption.



Figure 6: Percentage removal of Total-N in effluent with time(CCF-Coconut coir fibre;RS-Rice straw;SC-Saw chips;RH-Rice husks;1-Experimental series 1;2-Experimental series 2)



Figure 7: Concentration of Cl<sup>-</sup> in effluent with time(CCF-Coconut coir fibre;RS-Rice straw;SC-Saw chips;RH-Rice husks;1-Experimental series 1;2-Experimental series 2)

### 4. Conclusions

In the laboratory-scale column experiment, different degrees of contaminant removal were shown by different reactive media, namely coconut coir fibre, rice straw, saw chips and rice husks. The percentage removal of organic matter, chloride and nitrogenous compounds by all media were satisfactory. Adsorption and biological uptake could be the major treatment mechanisms of organic materials and ammonia in all media. Rice straw and saw chips performed the best in removing organic materials through adsorption. Coconut coir fibre and rice husks were the best supportive media for biological uptake of organic matter while rice husks were the best supportive media for nitrification. Adsorption could be the dominant mechanism for chloride removal in all media. All media equally supported the chloride removal. The reactivity of the organic materials depends on the ability or availability of the contained carbon and according to the study of Waybrant et al. (1995), the combination of more than one organic source is more successful than the use of solely one material. This is due to

the fact that a mixture of organic materials contains compounds with varying complexity, some of them decomposing fast and others in a long time period, thus achieving long term reactivity of the barrier. For reliable expectation on the longevity of PRBs, column test has to be performed for longer periods of time and the changes in material reactivity have to be carefully observed (Park et al., 2002). Therefore the importance of carrying out column experiments with mixed reactive media for prolonged periods is highlighted to achieve better results.

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