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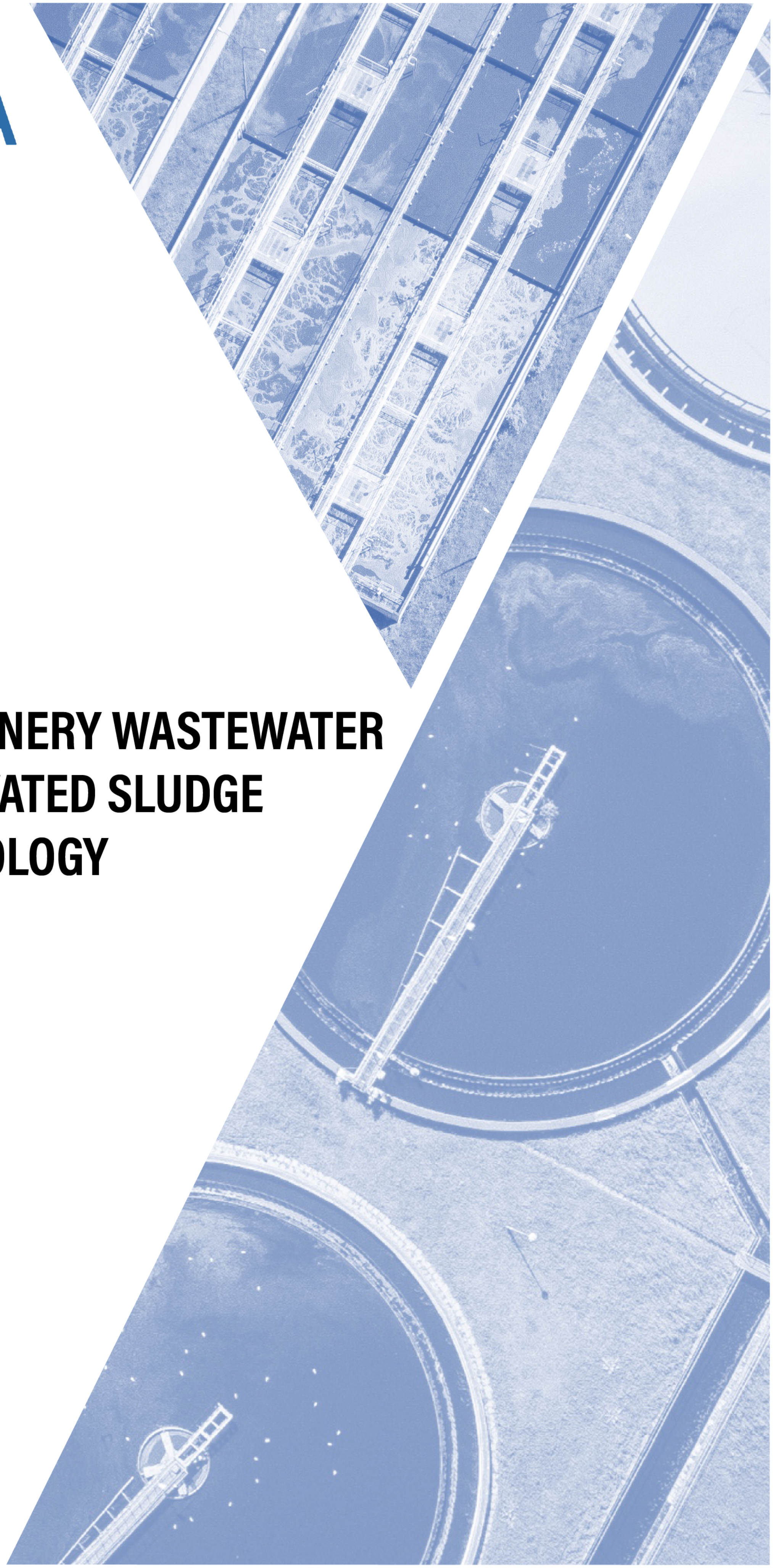

Excerpt from:

TREATMENT OF REFINERY WASTEWATER USING KENAF/ACTIVATED SLUDGE TREATMENT TECHNOLOGY

Research Report of

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TABLE OF CONTENTS

List of Figures

1) BACKGROUND

The refining process consumes large amounts of water and consequently significant volumes of wastewater are generated. These wastewaters have been recognized as hazardous industrial waste since they contain toxic substances such as phenols, hydrocarbons, sulfides, ammonia, and heavy metals. The presence of these toxic compounds poses significant challenges to the efficiency and stability of wastewater treatment processes.

Treatment of industrial wastewater by biodegradation has been an important waste management process for many years (DeFilippi and Lewandowski, 1998). Biodegradation of contaminants in wastewater is currently the most economical and efficient means for eliminating pollutants. However, different methods are employed to achieve the contact between the microbes and the wastewater contaminants. Both suspended growth and fixed film processes have been used.

Activated sludge systems can be operated at high sludge recycle ratios to achieve both high biomass concentrations within the reactor, and minimize biological solids formation. However, the effectiveness of sludge recycling is limited by the efficiency of the clarification step. Additionally, long sludge ages can result in bio-accumulation of inhibitory compounds, which limit the biodegradation and flocculation efficiency. Therefore, difficulties are often encountered in activated sludge plants that attempt to lower sludge production by increasing sludge age. The major problems encountered with this approach are the inability to settle the large solids inventory in the clarifier, which results in a very high sludge bed.

1.1 Fixed-Film Systems

Fixed-film bioreactors for treatment of industrial wastewater have recently gained acceptance (DeFilippi and Lewandowski, 1998 and Bernard, 1990). The fixed-film bioreactor is a ‘secondary’ aerobic system used in the biological degradation of organic pollutants in industrial wastewater. Advanced fixed-film bioreactors can be constructed in a variety of configurations that include rotating biological contactors, fluidized beds and packed beds, and microporous membranes.

Fixed-film bioreactors with rotating disks or packed beds appear to produce the greatest efficiency and stability, especially when a high degree of degradation is desired. Regardless of the configuration, these systems exhibit characteristics that give them advantages over more conventional suspended growth reactors such as activated sludge systems, and the low performance fixed-film systems such as trickling filters.

1.2 Kenaf Bio-Media

Kenaf Bio-Media is a natural microbial support material. When added to a suspended growth wastewater treatment process, it acts as a support medium for biofilm development. This can improve settling and biomass retention characteristics of the process, which allows better solids recycle and can allow for longer apparent solids retention times and reduce biological sludge production. The sorptive nature of the Kenaf can increase moderation of organic shock loads, and reduce the likelihood of process upsets. Unlike plastic support media, which are commonly utilized in the refinery wastewater treatment industry, Kenaf is biodegradable and can be more efficiently disposed of after its useful lifetime.

The Kenaf fixed-film system has four principal advantages over many of the other currently available systems:

1) It is simpler to operate.
2) It moderates shock loads with greater efficiency than plastic media.
3) It forms less solid wastes.
4) It is more energy efficient, or it requires less power to operate.

Kenaf in Briquette Form

2) OBJECTIVES

To evaluate the feasibility of using the Kenaf as a bio-media where it could be used to retrofit the current activated sludge systems and make them into partially - fixed film systems.

To accomplish this overall goal, the following research questions must be answered:

- Does Kenaf's absorption ability help with BTEX, phenols, hydrocarbons, ammonia?
- Can Kenaf help control H2S through absorption?
- How long will it take to grow a viable sustainable biofilm on the Kenaf?
- Will the Kenaf allow the activated sludge system to handle increases in organic loadings?
- Will you see increased process stability and resistance to shock loading?
- Does Kenaf help lower Oxygen demand?
- Does Kenaf increase settleability in the clarifier as other fixed film processes do?
- Does Kenaf help achieve easier sludge dewatering and handling?
- Does the biofilm slough off and lose its ability to be effective? If so, what is its lifecycle?

Kenaf after immediate addition into activated sludge system. The kenaf briquettes dissolve into solution.

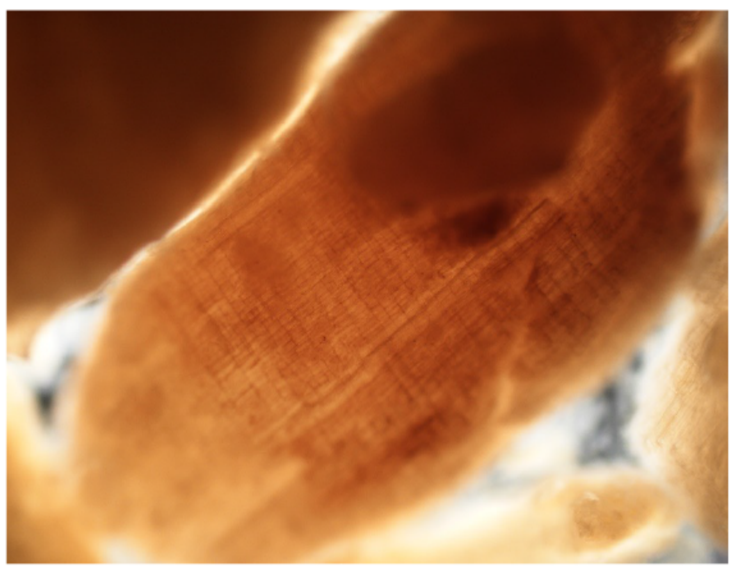
3.1 Adsorption Studies - Isotherms and other adsorption tests were used to determine the rate and degree of Kenaf adsorption in the treatment of Refinery Wastewater.

a) **Batch Kinetic Rate Studies.** Batch Kinetic Rate studies were conducted to establish equilibrium time for isotherm tests. (Equilibrium time for isotherm testing and data for scale up.) Kinetic rate studies were conducted using sodium azide sterilized, Kenaf bio-media. The azide-sterilized Kenaf bio-media was used as an “abiotic control”. This allowed determination of whether COD and target chemical compounds are being removed by Kenaf bio-media via sorption mechanisms. It also revealed the degree of compound removal and the removal capacity of Kenaf bio-media.

b) **Isotherm Testing** Isotherm experiments were conducted using 250 mL Erlenmeyer flasks which were charged with Kenaf bio-media masses ranging from 0.1 to 50.0 grams and were filled with 100 mL of test organic solution. The data obtained from the batch isotherms were analyzed using the standard Freundlich isotherm model.

A Comparison of organics removal by biologically active Kenaf bio-media to that of sterilized Kenaf bio-media was used to assess the relative importance of biological mechanisms for organics removal in the Kenaf/Biomass system.

Biofilm Development on Kenaf Particle



Biofilm Growth on Kenaf - Under Microscope

3.2 SRT Optimization

The pilot scale activated sludge systems were operated at SRTs of between 5 and 20 days to determine the optimum SRT/MLVSS to achieve the best possible effluent. Effluent samples were analyzed for organics, COD, ammonia, and sulfide. Waste MLSS was analyzed for TSS, VSS, OUR, ATP, and dewaterability by capillary suction test. At least 20 days of steady state operation were used to obtain the kinetic parameters. Aliquots of the MLSS were removed for SVI testing and returned to the system after 30 minutes. SVI testing was performed to assess settleability.

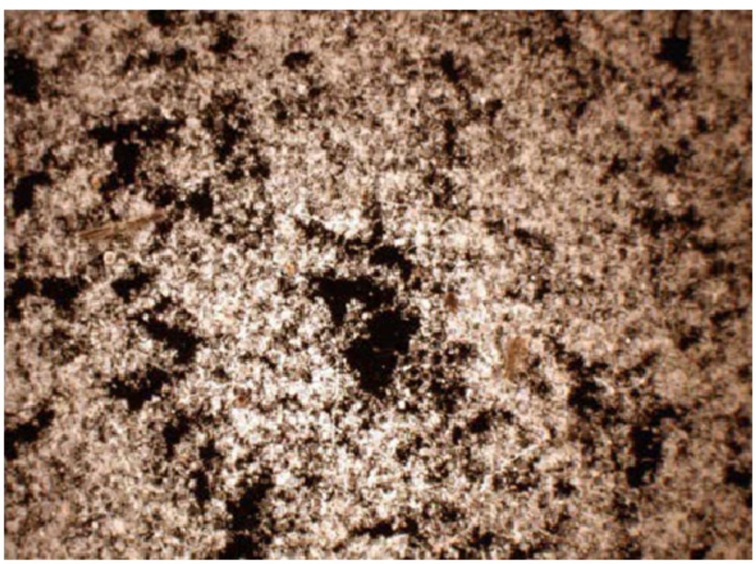
3.3 Shock Loadings

To assess the ability of the Kenaf to moderate the severity of shock loadings, the Activated sludge units (Kenaf and controls) were subjected to a series of increasing loadings. Increased organic loading rates were obtained by spiking the wastewater with the target compounds (phenols, BTEX, and hydrocarbons in the same proportions as present in the refinery wastewater). The biomass health was assessed using ATP and OUR measurements, substrate removal and settleability measurements (i.e., SVI index).

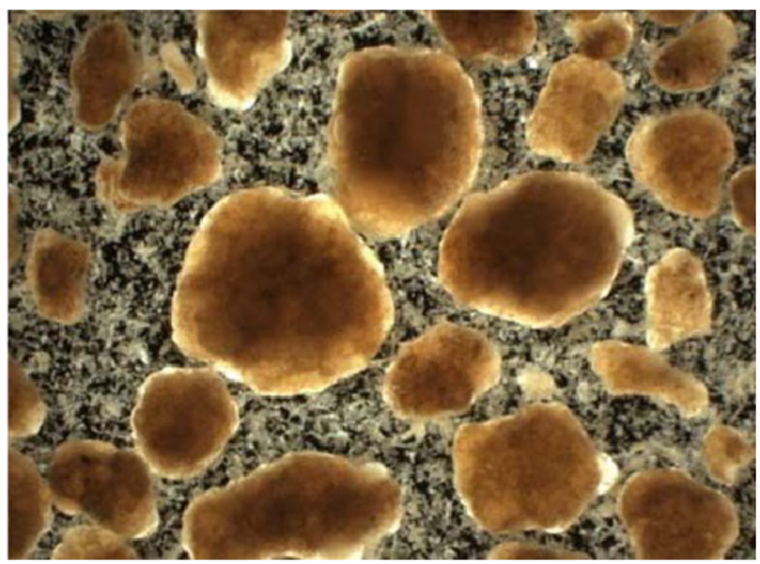
4) RESULTS

Isotherm testing was conducted on refinery wastewater to determine the ability of Kenaf to absorb/adsorb various inhibitory constituents from the actual refinery wastewater matrix. Wastewater from three refineries (Exxon, Citgo, and Chevron) were collected and used for isotherm testing. Isotherm tests were conducted in triplicate and the averages for each wastewater were plotted to determine the values of Freundlich isotherm constants.

The results of Freundlich isotherm testing are presented graphically in Figures 1 through 10, and summarized in Table 1. From the figures as a whole, several facts are apparent. First, the linear plots of log concentration versus log of the mass sorbed by the Kenaf (X/M) shows that sorption of the individual chemical constituents of refinery wastewater appears to be well modeled by the Freundlich Isotherm model. Secondly, the affinity of the Kenaf for the individual refinery wastewater compounds is relatively high and is comparable or slightly lower than typically reported for activated carbon. Finally, while the sorption of all compounds are high in all three refinery wastewaters tested, there were significant differences between a numbers of the analytes.



Conventional Activated Sludge



Aerobic Granules in Kenaf Based System

4.1 Aniline

The Freundlich Isotherm for Aniline is shown in Figure 1. The Kenaf showed a large affinity for sorbing aniline from all three wastewaters. The isotherm for the Exxon wastewater had the lowest degree of sorption at all equilibrium concentrations. Citgo and Chevron wastewaters showed similar degrees of sorption, which were almost two times higher than for the Exxon wastewaters at all concentrations. Kenaf would be useful in reducing the concentration of aniline in all three waste waters. Since aniline is inhibitory to both COD removal and nitrification, Kenaf could be highly effective in reducing process inhibition and also potentially lower the effluent concentration of aniline.

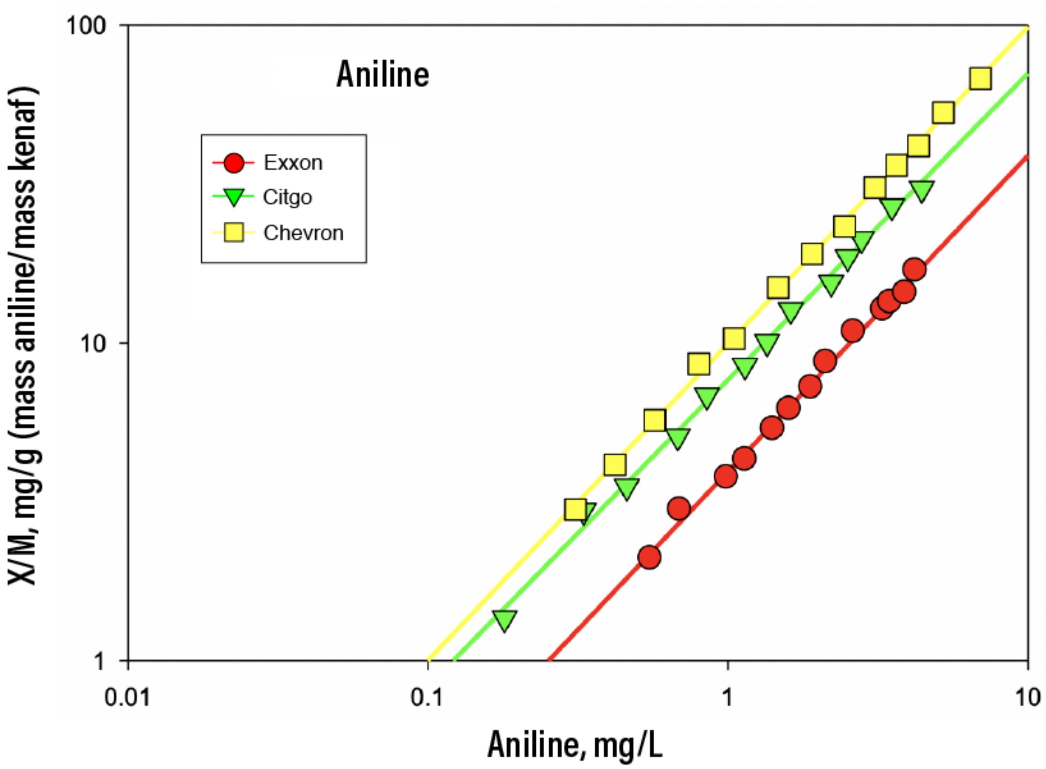


FIGURE 1. Freundlich Isotherms for Aniline Sorption by Kenaf

Nearly ideal (linear) sorption of aniline on Kenaf

4.2 Benzene

The Freundlich Isotherms for Benzene in the three wastewaters are shown in Figure 2. Benzene is inhibitory to wastewater biology when it builds up in the biomass to high concentrations and can cause nitrification problems at levels of slightly less than 10 ppm in un-acclimated systems. Kenaf showed a high affinity for benzene in all three wastewater matrices, and the degree of sorption exceeded that typically reported for activated carbon indicates that Kenaf has a good affinity for benzene.

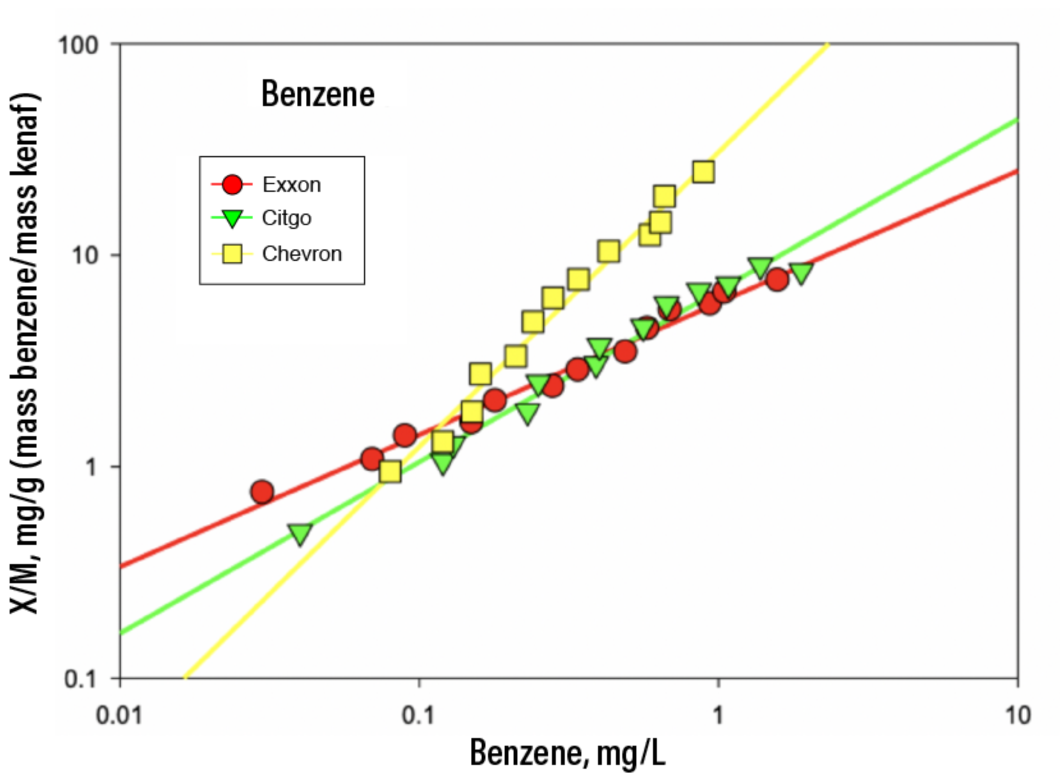


FIGURE 2. Freundlich Isotherms for Benzene Sorption by Kenaf

Good affinity for benzene by Kenaf

4.3 Decane & Eicosane

The Freundlich isotherms for Decane and Eicosane, two common alkanes found in refinery wastewater are shown in Figure 3 and 4. The sorption of these two alkanes were similar in all three matrices, and were extremely high. The highest measured sorption exceeded 200 mg/gram, which indicates Kenaf sorption of over 20% of its weight in these compounds. Since large amounts of these, and alkanes that lie between the two in size, can be present in refinery wastewater as dissolved and non-aqueous phase liquids (known as free-product), the high sorptive capacity could prove invaluable for refinery wastewater treatment processes.

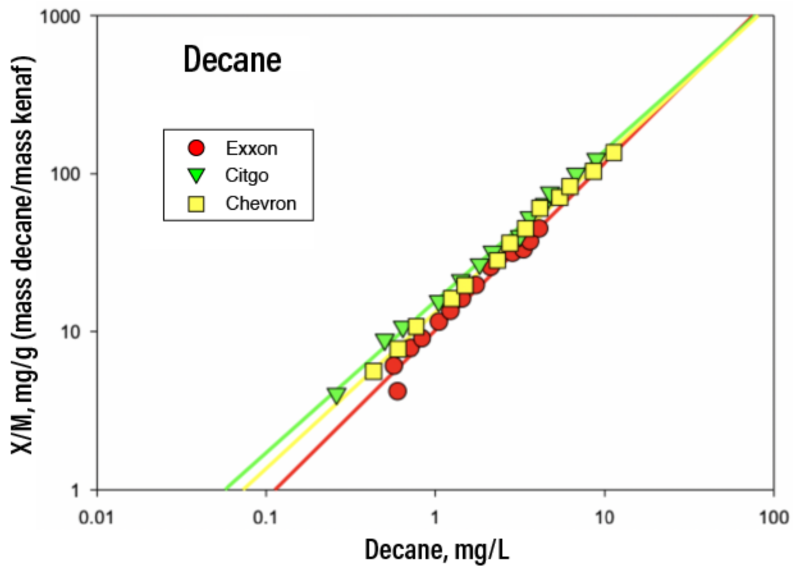


FIGURE 3. Freundlich Isotherms for Decane Sorption by Kenaf

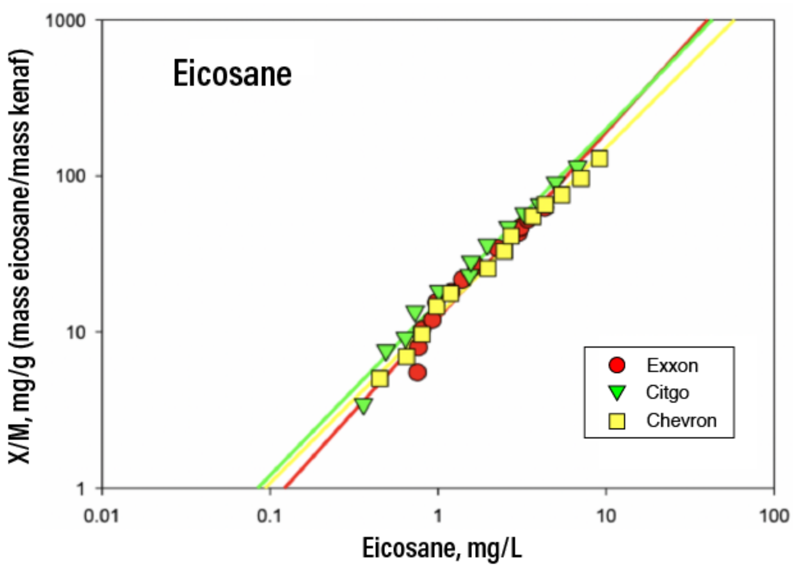


FIGURE 4. Freundlich Isotherms for Eicosane Sorption by Kenaf

Kenaf sorption of 20%+

4.4 Naphthenic

The Freundlich isotherms for Naphthenic acids are shown in Figure 5. Naphthenic acids are very inhibitory to aerobic heterotrophic bacteria that remove biochemical oxygen demand (BOD) when present at concentrations above 5 ppm. Even lower amounts can cause inhibition or cessation of nitrification processes and cause effluent toxicity. The Kenaf had a significant ability to absorb naphthenic acids from all three refinery wastewaters. This was similar to the degree of sorption attained using activated carbon. This means that the Kenaf could absorb a large amount of these chemicals and could help reduce process inhibition. This indicates a good affinity for sorbing naphthenic acids at low aqueous phase concentrations and a high affinity when aqueous phase concentrations were well above 1 ppm.

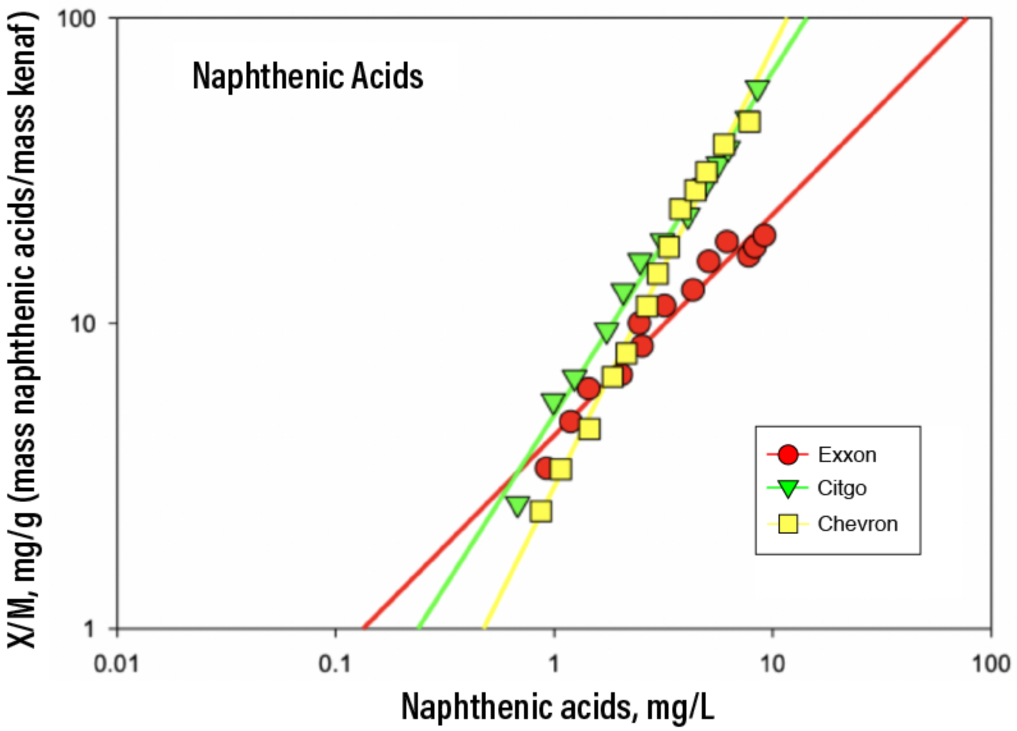


FIGURE 5. Freundlich Isotherms for Naphthenic Acids Sorption by Kenaf

Kenaf sorption of naphthenic acids can reduce biological process inhibition

4.5 Cresol

Isotherms for o-cresol and p-cresol are shown in Figures 6 and 7. These substituted phenols are inhibitory to nitrification processes at levels as low as 2 mg/L and can inhibit BOD removal processes when present above 10 mg/L. Both o-cresol and p-cresol are common causes of refinery nitrification process inhibition. The Kenaf had a high affinity for o-cresol and a similarly high affinity for p-cresol. This means that the Kenaf would be very effective for reducing the concentration of cresols in the refinery wastewater treatment process.

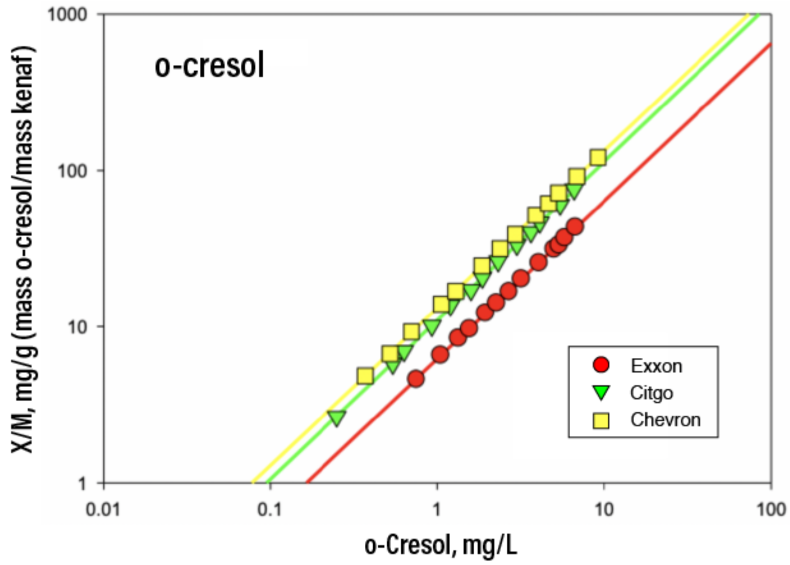


FIGURE 6. Freundlich Isotherms for o-Cresol Sorption by Kenaf

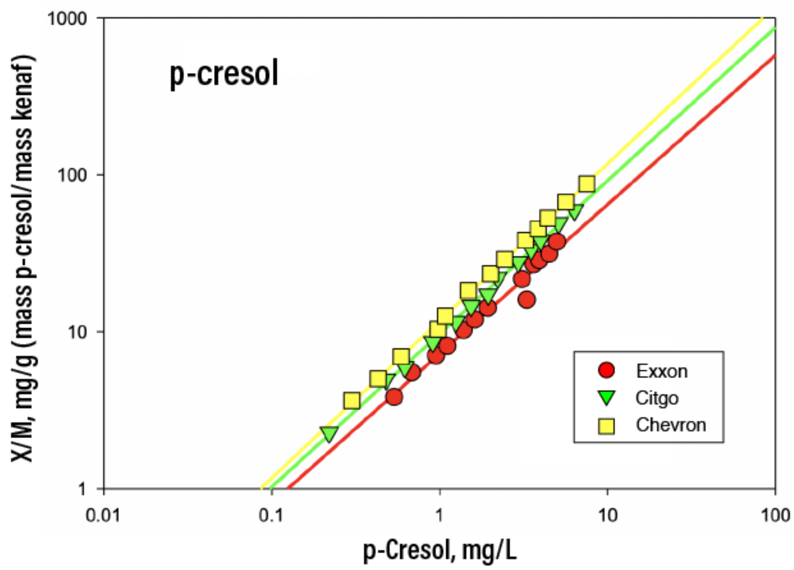


FIGURE 7. Freundlich Isotherms for p-Cresol Sorption by Kenaf

Kenaf has high affinity for cresols

4.6 Phenol

Isotherms for sorption of phenol onto Kenaf are shown in Figure 8. Phenol can inhibit nitrification at concentrations between 5 and 10 mg/L and will inhibit BOD removal at much higher concentrations. Sorption of phenol from all three wastewaters was fairly consistent. This indicates that the Kenaf has an exceptionally high affinity for phenol.

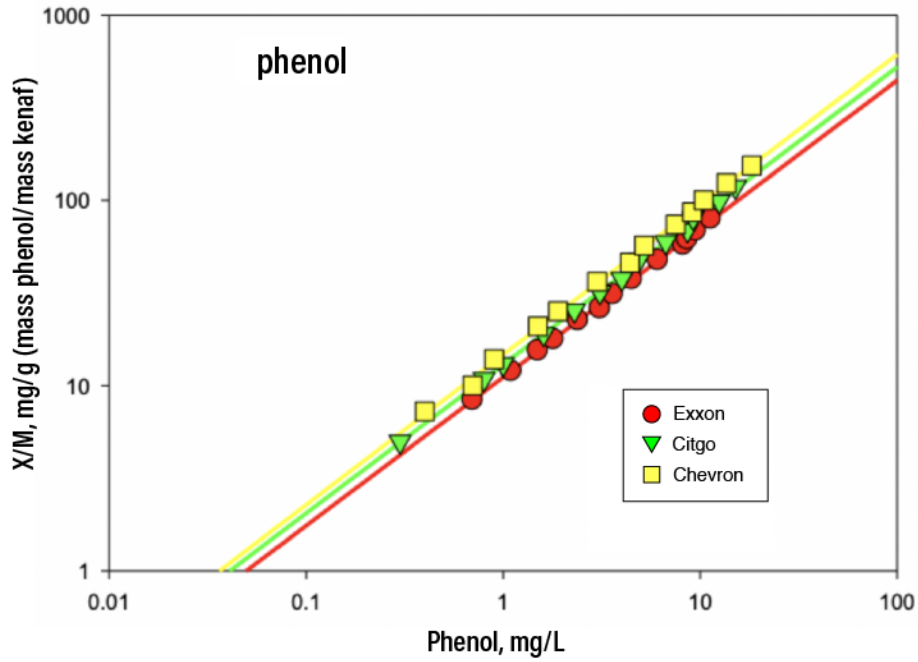


FIGURE 8. Freundlich Isotherms for Phenol Sorption by Kenaf

Isotherms for sorption of toluene and octadecane are shown in Figures 9 and 10.

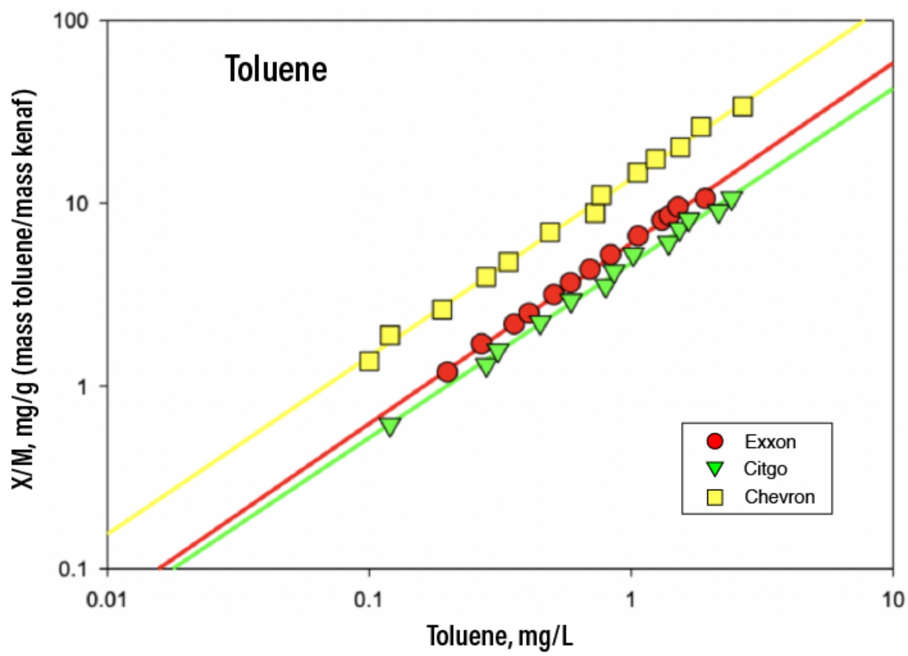


FIGURE 9. Freundlich Isotherms for Toluene Sorption by Kenaf

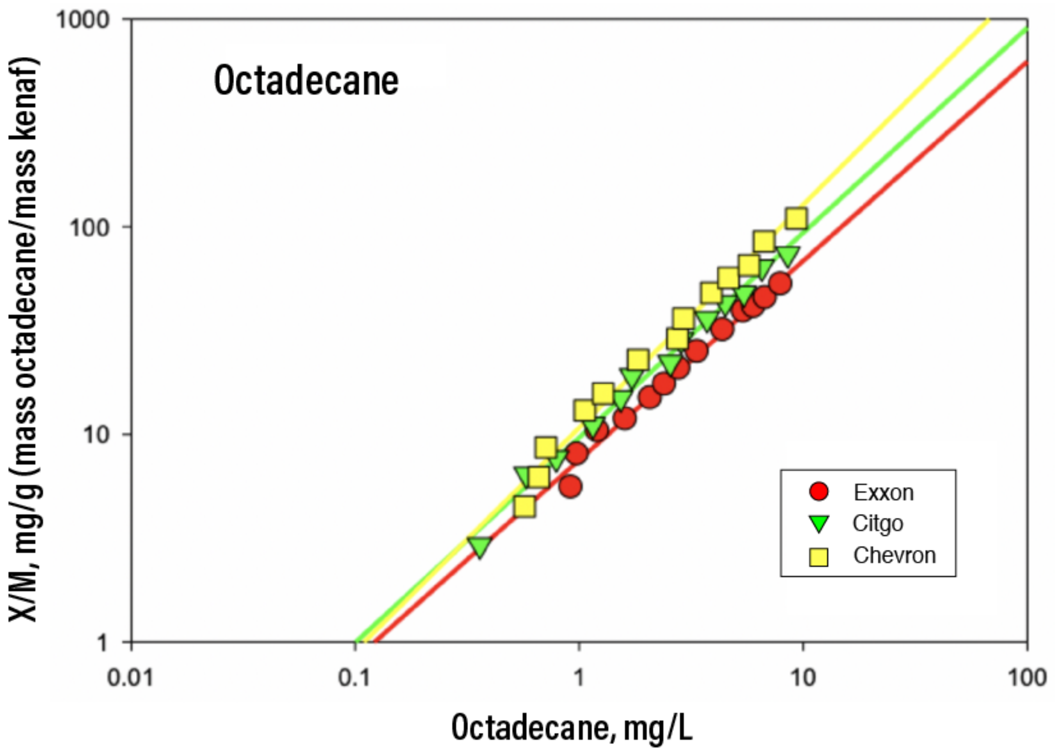


FIGURE 10. Freundlich Isotherms for Octadecane Sorption by Kenaf

4.7 Desorption Through Biodegradation

It is important to note that sorption by Kenaf was highly reversible. When solids were removed from the isotherm tests and placed into distilled water, a significant portion of the chemical would desorb into solution. This means that absorbed compounds would likely be available for biodegradation by microorganisms in the process. This could be very important, since desorption and biodegradation would play a crucial role in extending the life/capacity of the Kenaf in the process.

TABLE 1. Summary of Freundlich Isotherm Constants for Various Refinery Waste Chemicals

		Exxon	Citgo	Chevron
Aniline	K_f	3.6	7.8	9.5
	n	0.96	0.97	0.99
Benzene	K_f	4.1	6.8	3.0
	n	0.79	0.77	1.23
Decane	K_f	10.11	15.39	13.20
	n	1.06	0.97	0.98
Eicosane	K_f	12.23	15.52	12.78
	n	1.19	1.10	1.07
Naphthenic Acid	K_f	4.46	5.01	3.09
	n	0.75	1.15	1.24
o-cresol	K_f	6.24	10.96	13.20
	n	1.01	1.02	1.01
Octadecane	K_f	7.52	9.55	10.72
	n	0.96	0.99	1.08
p-cresol	K_f	7.24	9.54	11.75
	n	0.96	0.98	1.00
phenol	K_f	10.96	12.88	14.72
	n	0.83	0.85	0.85
Toluene	K_f	5.98	4.70	13.49
	n	0.97	0.96	0.98

4.8 Colonization of Biomass

As a means of comparison, the rate and degree of colonization of biomass onto plastic media was determined and is presented in Figure 11. Inspection of this figure indicates that there was a significant amount of growth occurring over the first six (6) days after inoculation. At six days, there was between 200 and 300 micrograms of ATP present per gram of media. This means that there was between 200 and 300 mg of bacterial mass per gram of media. This is an expected value for biomass on plastic growth support media. It is important to note, that there was considerable variability between the three replicates, indicating the colonization is variable. After six days, there was little or no change in the amount of biomass on the media, indicating that a maximum density of growth had occurred.

The rate and degree of colonization of biomass on the Kenaf is shown in Figure 12. The amount of ATP increased much more quickly on the Kenaf during the first few days of incubation than was observed for the plastic media. The ATP concentration continued to increase throughout the 10 day incubation period, but was tapering off by day 10. The bacterial mass achieved a maximum level of between 500 and 600 micrograms per liter. This is over two times higher than the plastic support media and represents a very high degree of bacterial colonization. This test demonstrated the high rate and degree of bacterial colonization by refinery wastewater microorganism on the Kenaf.

Kenaf biomedia (top) and the equivalent surface area of plastic media

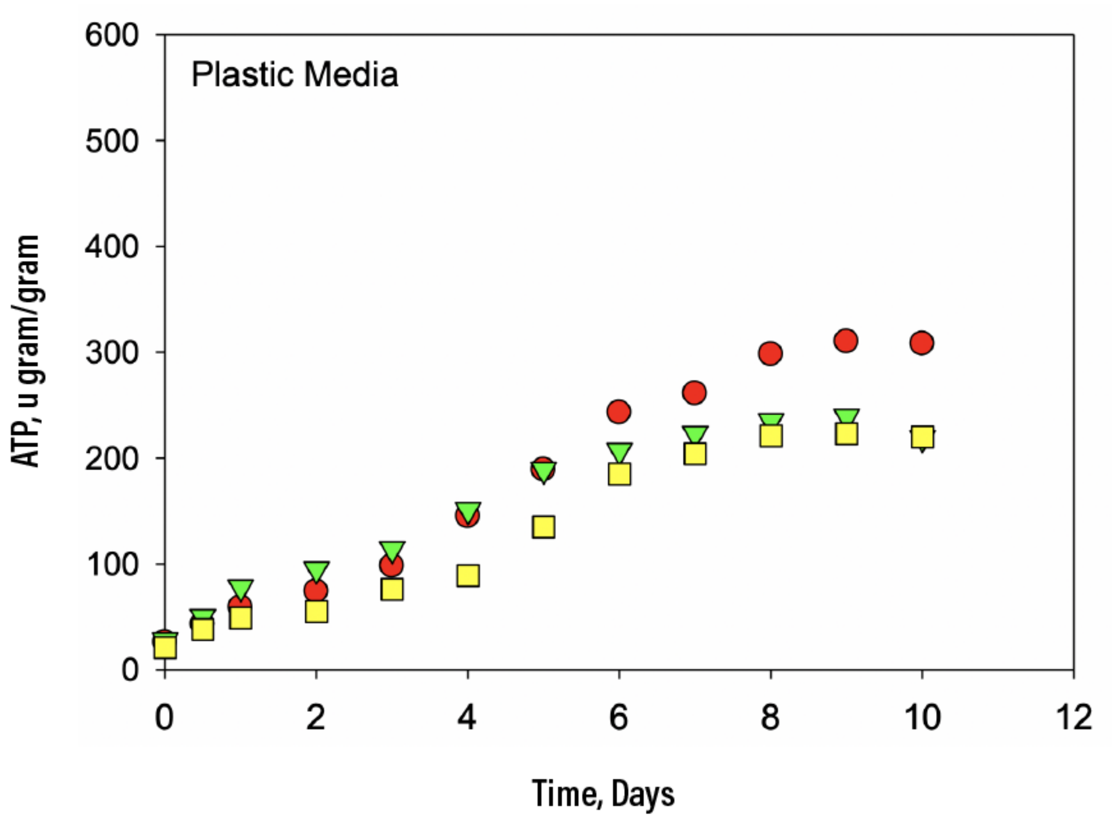


FIGURE 11. ATP content of Bacterial Biomass on Plastic Media over Ten Day Colonization Testing

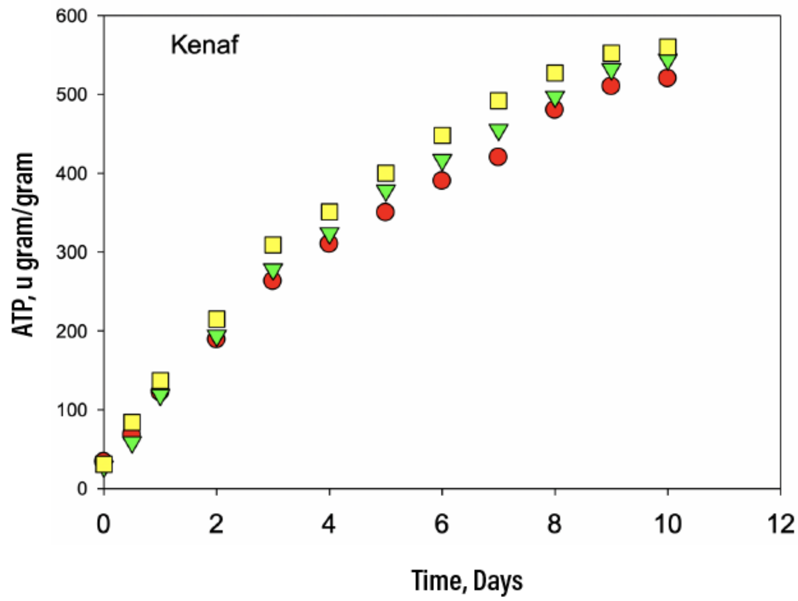


FIGURE 12. ATP content of Bacterial Biomass on Ground Kenaf over Ten Day Colonization Testing

Figure 13 shows a comparison of the ATP present for plastic media and Kenaf.

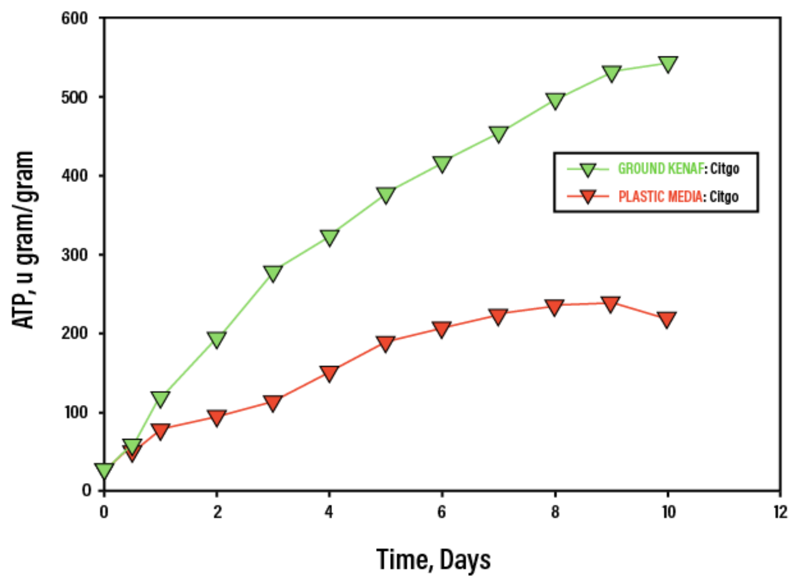


FIGURE 13. ATP Content of Bacterial Biomass on Plastic Media & Ground Kenaf over 10 Day Colonization Testing

Two times biomass on Kenaf vs plastic

4.9 Reactors Treating a Defined Synthetic Refinery Wastewater

To test the efficacy of Kenaf for decreasing the impact of refinery wastewater on activated sludge treatment processes, laboratory reactors were operated with a hydraulic residence time (HRT) of ½ day and a mean cell residence time (MCRT) of 10 days. These were chosen as average values for refinery wastewater treatment processes. The reactors were seeded with 1,800 mg/L of RAS from an oil refinery using nitrifying activated sludge. The test reactors received 1,000 mg/L of Kenaf, while the control reactors had no Kenaf added. The influent was a refinery wastewater with a COD of 4,000 mg/L and a BOD of 2,700 mg/L. The influent contained 150 mg/L of phenols, 75 mg/L of cresols (approx. half o-cresol and half p-cresol), 450 mg/L of alkanes, 80 mg/L of BTEX, and 120 mg/L of ammonia nitrogen. Three control reactors and three test reactors were operated, and the averages of the daily values were used for comparison.

4.10 COD & BOD

The average MLSS and COD for the control reactors and Kenaf reactors are shown in Figure 14. The MLSS and BOD for the control reactors and Kenaf reactors are shown in Figure 15.

The control reactors were seeded at 1,800 mg/L of MLSS. The MLSS increased over the first ten days of operation, reaching a quasi-steady-state value of 2,100 mg/L, which remained relatively consistent (+/- 100 mg/L) for the remainder of the 100 day testing period. The COD of the reactor started at 1,250 mg/L, which was much lower than the influent COD due to the dilution by the seed. The COD decreased to 700 mg/L by day ten and remained at that level until about 40 days after operation began. After 40 days, the COD began to slowly increase, reaching almost 900 mg/L by the end of the 100 day test period. Similarly, the BOD decreased from an initial concentration of 700 mg/L to 80 mg/L by the 10th day. This represents almost 97 percent removal of BOD. After 50 days of operation, the BOD began to slowly increase, reaching almost 200 mg/L by the end of 100 days. While this is still 95 percent removal of the influent BOD, the slow increase of BOD (and COD) indicates that the process is slowly declining.

The Kenaf was inoculated with biomass and colonized for 10 days prior to the beginning of reactor operation. The Kenaf reactors received 1,800 mg/L of colonized Kenaf at the onset of operation. The MLSS increased over the first 10 days of operation to 2,250 mg/L and remained within 100 mg/L of this level for the remained of the study. The initial COD was 1,300 mg/L on day zero. The COD decreased rapidly over the first few days of operation, reaching a steady-state concentration of 350 mg/L by day 10. The COD remained between 350 and 400 mg/L for the remainder of the 100 day study. On visual inspection, it appears possible that the COD is slowly increasing over the last 50 days. The BOD was initially 700 mg/L, and decreased quickly over the first 5 days. By day 15, the BOD was less than 25 mg/L and remained at that level for the rest of the testing period.

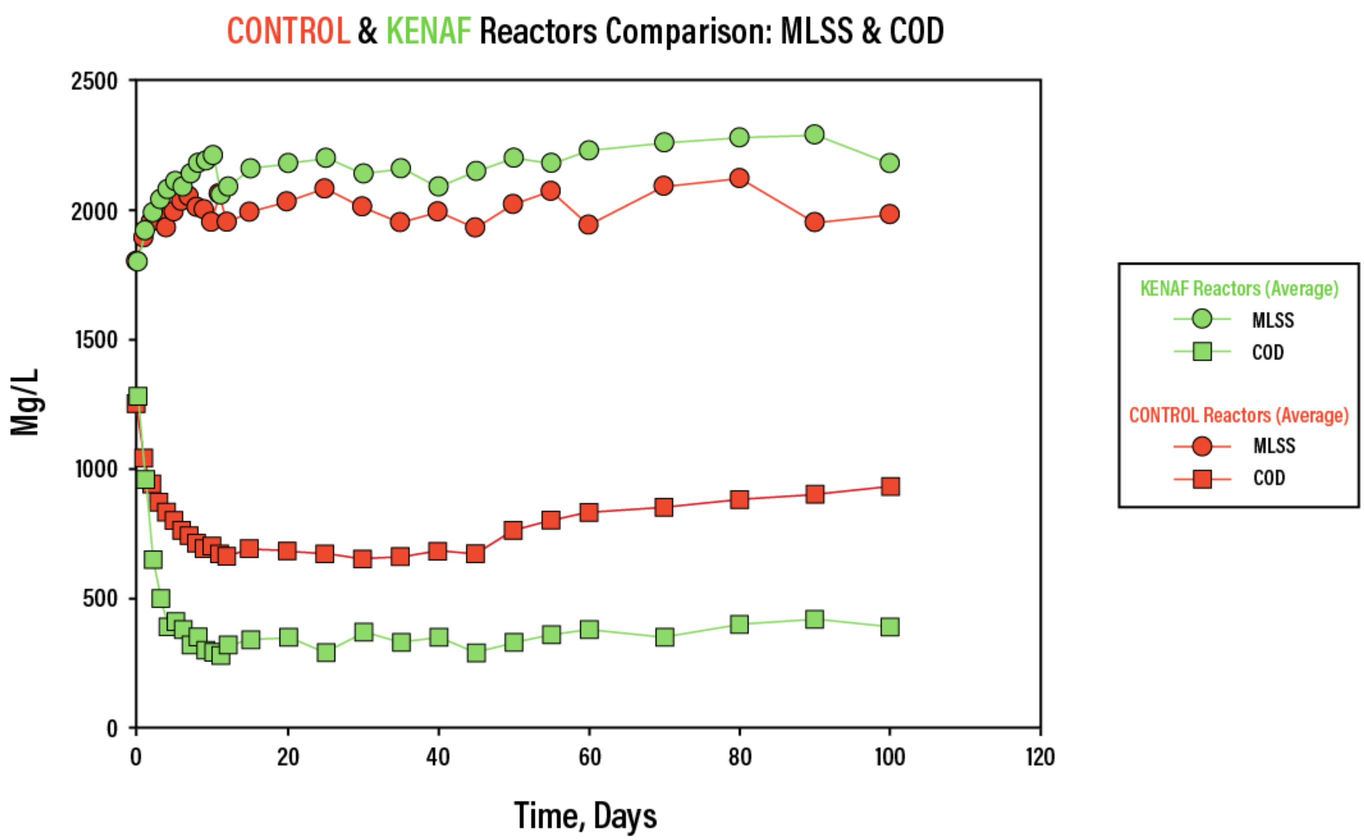


FIGURE 14. Average MLSS & COD
in Control & Kenaf Activated Sludge Reactors Receiving Refinery Wastewater

Superior COD removal performance by Kenaf reactor

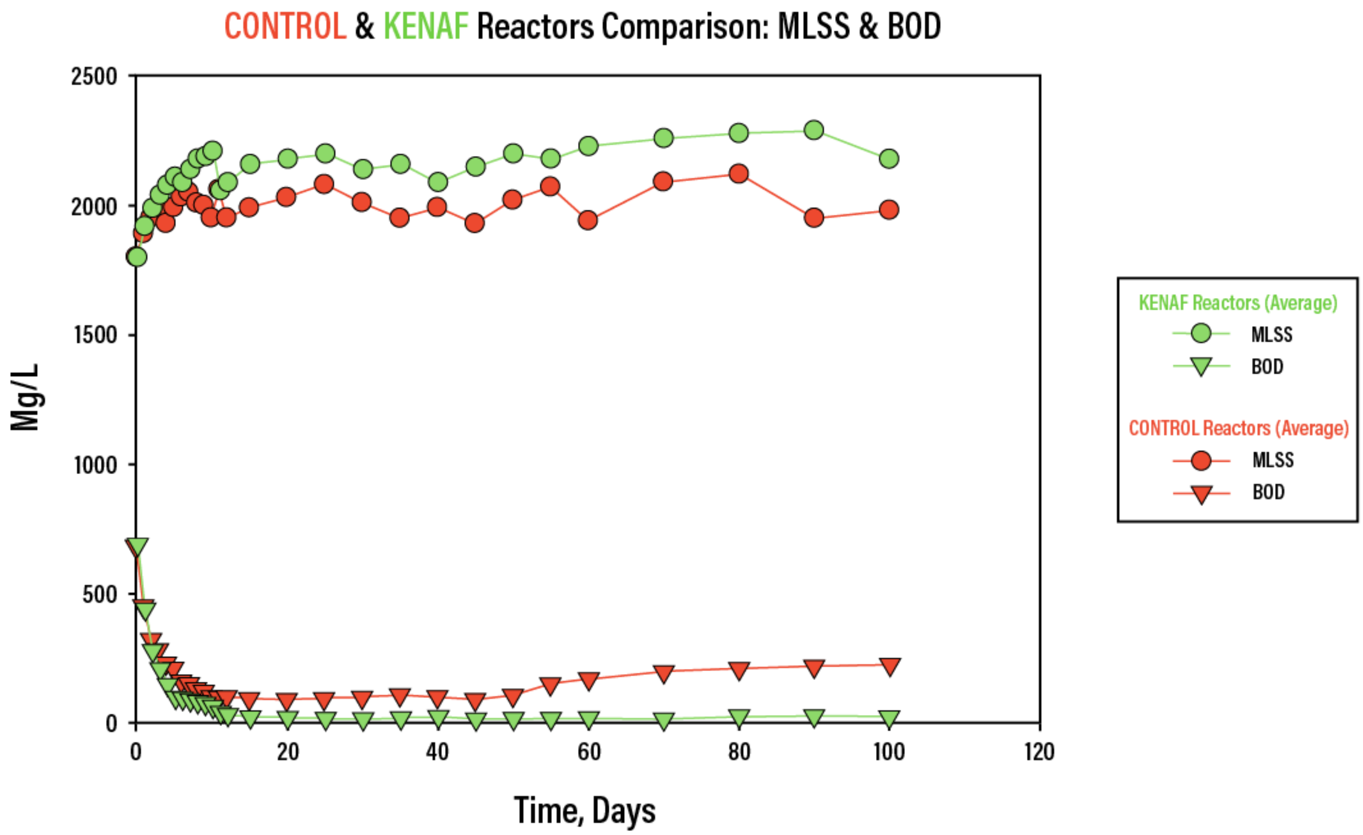


FIGURE 15. Average MLSS & BOD
in Control & Kenaf Activated Sludge Reactors Receiving Refinery Wastewater

Superior BOD removal performance by Kenaf reactor

The addition of the Kenaf to the activated sludge processes treating refinery waste had a beneficial effect on the process. With Kenaf, the reactors achieved steady-state quicker than the control reactors. The steady-state levels of COD and BOD in the effluent of the Kenaf reactors were significantly lower than the controls. The BOD with Kenaf was below 30 mg/L throughout the test period. This means that almost 99% reduction in soluble BOD was achieved. The lowest soluble effluent BOD achieved by the control reactors was 80 mg/L, which is three times higher than the Kenaf reactors. Furthermore, there was a slow decline in performance in all three control reactors, while no decrease in reactor performance was observed in any of the Kenaf reactors.

4.11 BTEX, Alkanes & Phenols

The concentrations of BTEX, alkanes, and phenols in the activated sludge reactors were determined for the control reactors and the Kenaf reactors (Figure 16, 17 & 18). During the first 15 days, the BTEX, phenols, and alkane concentrations in the control reactors decreased significantly, indicating that biodegradation of these compounds is occurring to a large degree of completion. After about 30 days of operation, the concentration of these compounds began to slowly increase, indicating that the biodegradation efficiency had begun to decline and these inhibitory compounds were beginning to accumulate in the process. The increase in BTEX, alkanes, and phenols parallels the increased in COD and BOD noted before. Phenols were higher than 50 mg/L after sixty days. At this concentration, the phenols in the control reactor are likely to inhibit nitrification and would be beginning to inhibit the BOD removal rate as well.

The levels of BTEX, alkanes, and phenols decreased quickly in the Kenaf reactors, reaching levels below 10 mg/L at steady-state. The rate and degree of decrease in the phenols and BTEX concentration was much higher than for the control reactor. The levels of these compounds did slowly increase over time, but never exceeded 20 mg/L. At these concentrations, the phenol and BTEX resultant levels in the Kenaf reactor would be unlikely to inhibit BOD removal. However, they are at the threshold for inhibition nitrification processes.

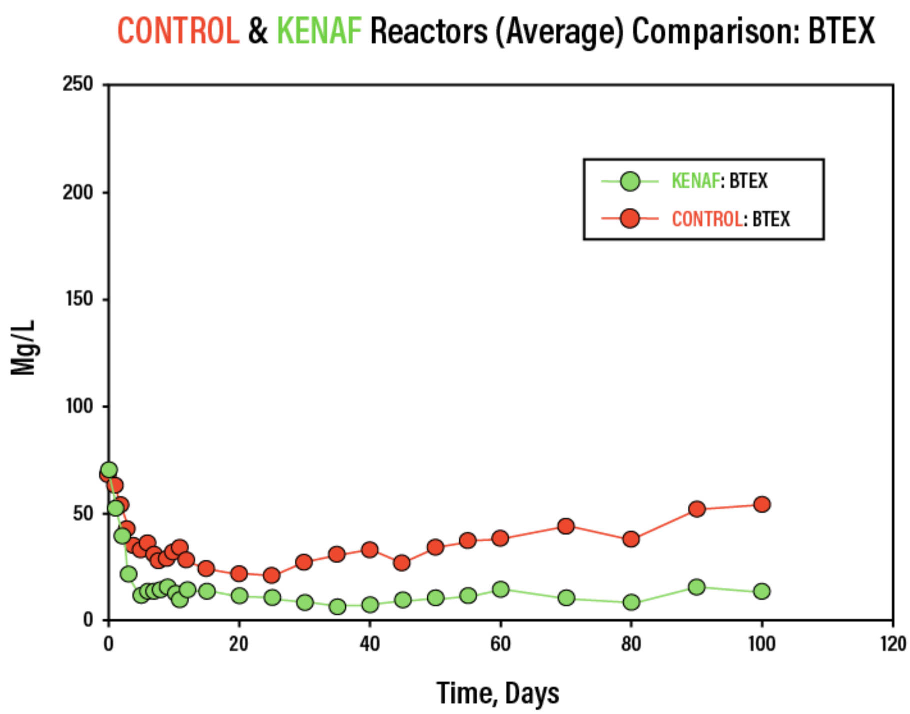


FIGURE 16. Average BTEX
in Control & Kenaf Activated Sludge Reactors Receiving Refinery Wastewater

Superior BTEX performance of Kenaf reactor

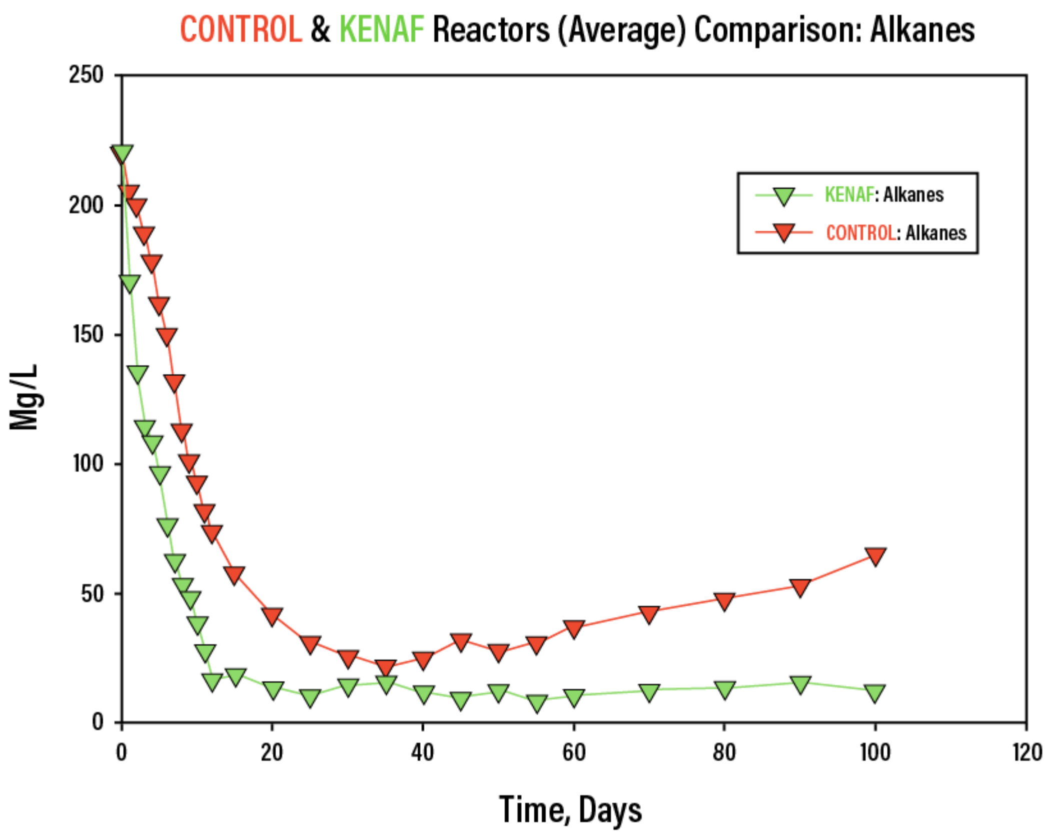


FIGURE 17. Average Alkanes in Control & Kenaf Activated Sludge Reactors Receiving Refinery Wastewater

Superior alkanes performance of Kenaf reactor

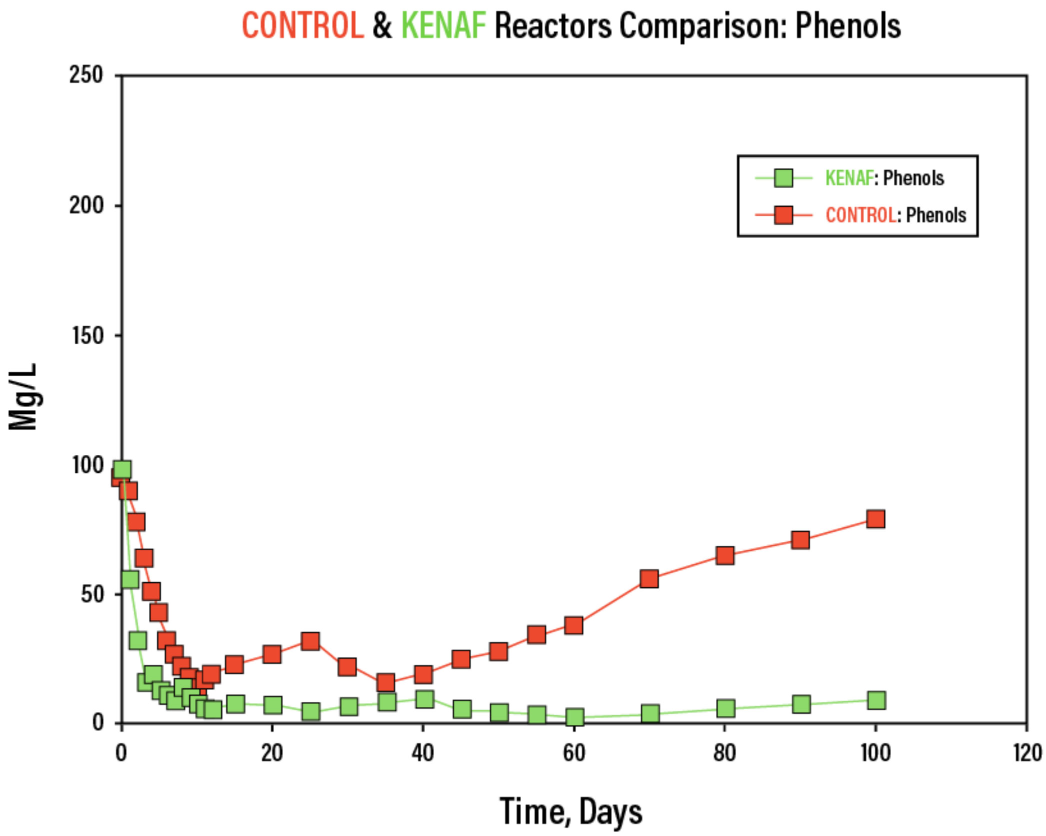


FIGURE 18. Average Phenols
in Control & Kenaf Activated Sludge Reactors Receiving Refinery Wastewater

Superior phenols performance of Kenaf reactor

4.12 Ammonia, Nitrite & Nitrate

The effluent ammonia nitrogen, nitrite-N, and nitrate-N were measured for the control reactor and Kenaf reactor, and are shown in Figures 19 & 20. In the control reactor, the ammonia concentration was initially 120 mg/L. Over the first 20 days of operation, the ammonia concentration began to decrease. This was partially due to uptake of ammonia nitrogen associated with the growth of biomass. Over the first ten days, no nitrite of nitrate was measured, indicating that nitrification was not occurring to a significant degree. Over the next thirty days, a small amount of nitrification occurred in the control reactor, as indicated by an increase in the concentrations of nitrite and nitrate.

However, nitrification was incomplete in the control reactor and unsteady based on the high ammonia concentration, high nitrite concentration, and low and variable nitrate concentration. Based on these results, nitrification of this refinery wastewater would be problematic at best, and likely would not be practical.

In the Kenaf reactor, the effluent ammonia nitrogen was initially 133 mg/L, and decreased steadily over the first 10 days of operation. By the 10th day, the ammonia nitrogen was less than 3 mg/L. A small spike in effluent nitrite nitrogen occurred around day eight, but only reached 4 mg/L in magnitude and rapidly decreased to less than 2 mg/L a few days later. The effluent nitrate-nitrogen was initially zero, and increased steadily, starting on day 6. By the twentieth day, the majority of the nitrogen was in the form of nitrate, with very little nitrite or ammonia present.

This shows that nitrification was proceeding in the reactors and was relatively complete. After about forty days, the ammonia concentration started to slowly increase over time with a concomitant decrease in nitrate. This indicates that the nitrification was possibly being inhibited to a small degree. The decrease in nitrification agrees well with the increase in the accumulated phenols and BTEX compounds in the biomass.

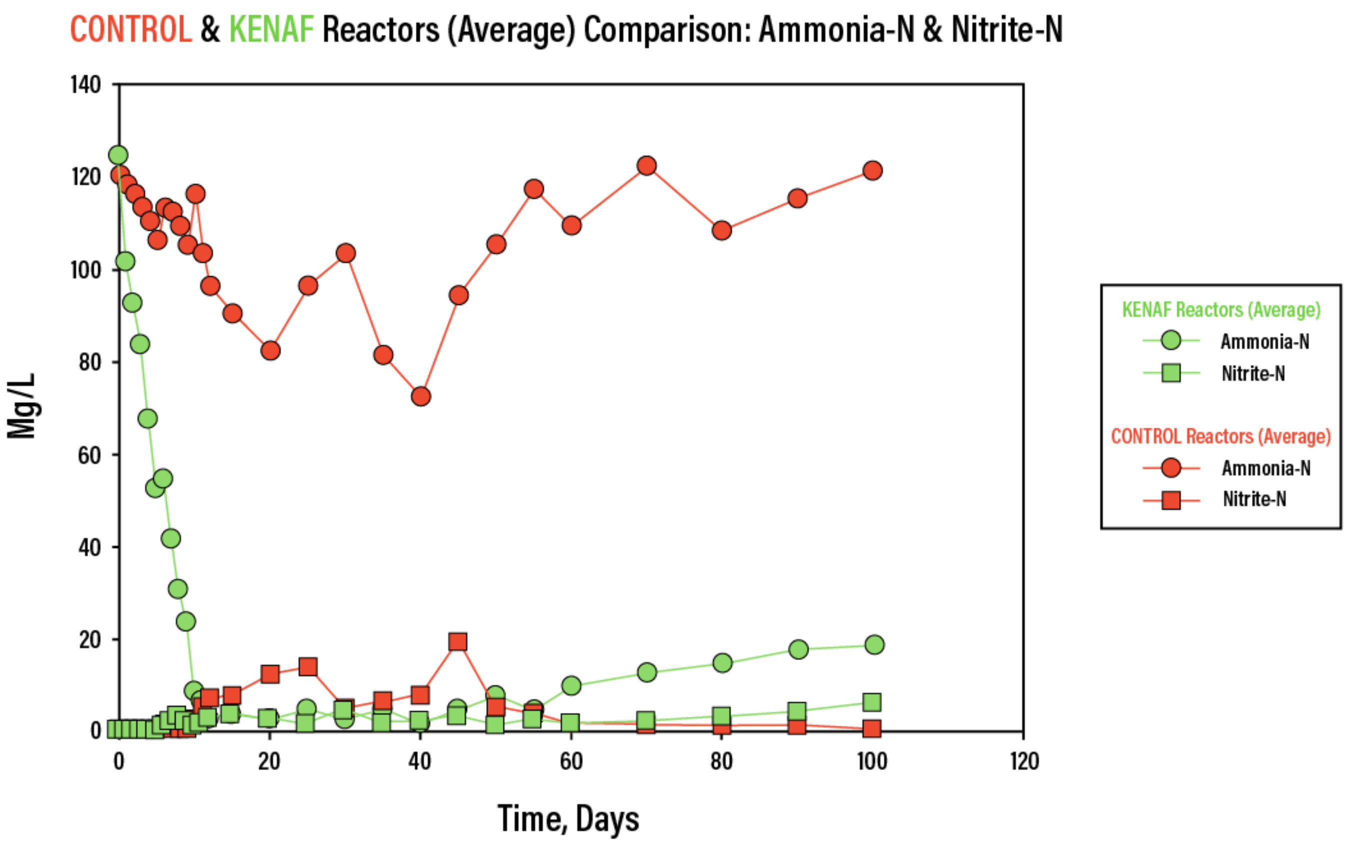


FIGURE 19. Average Ammonia-N & Nitrite-N
in Control & Kenaf Activated Sludge Reactors Receiving Refinery Wastewater

Nitrification with Kenaf process

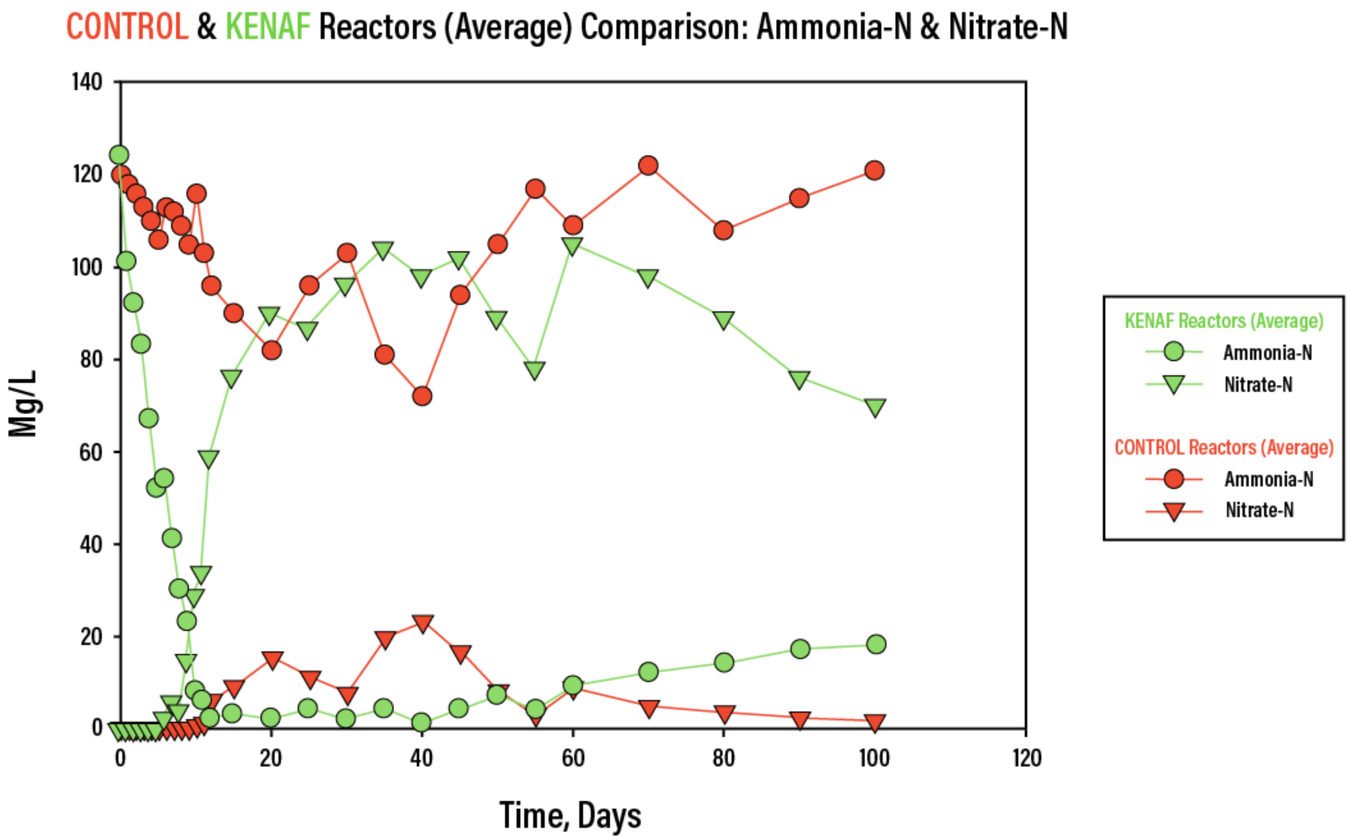


FIGURE 20. Average Ammonia-N & Nitrate-N in Control & Kenaf Activated Sludge Reactors Receiving Refinery Wastewater

Nitrification with Kenaf process, despite no nitrification in control reactors

4.13 Naphthenic Acids

Naphthenic acids are one of the more inhibitory compounds that is particular to refinery wastewater. The accumulation of naphthenic acids and their effects on nitrification were measured in a second set of activated sludge reactors.

The naphthenic acid concentration of the three replicate control reactors are shown in Figure 21. As shown in this figure, the naphthenic acids slowly accumulated in the biomass, reaching an ultimate concentration that was twice that of the influent. This indicates that the naphthenic acid is being bio-accumulated to a significant degree over a period of between 40 and 50 days. After this time, the concentration was relatively stable. At a level of approximately 20 mg/L, the naphthenic acids would likely be moderately inhibitory to the BOD degrading biomass, and almost certainly would inhibit nitrification.

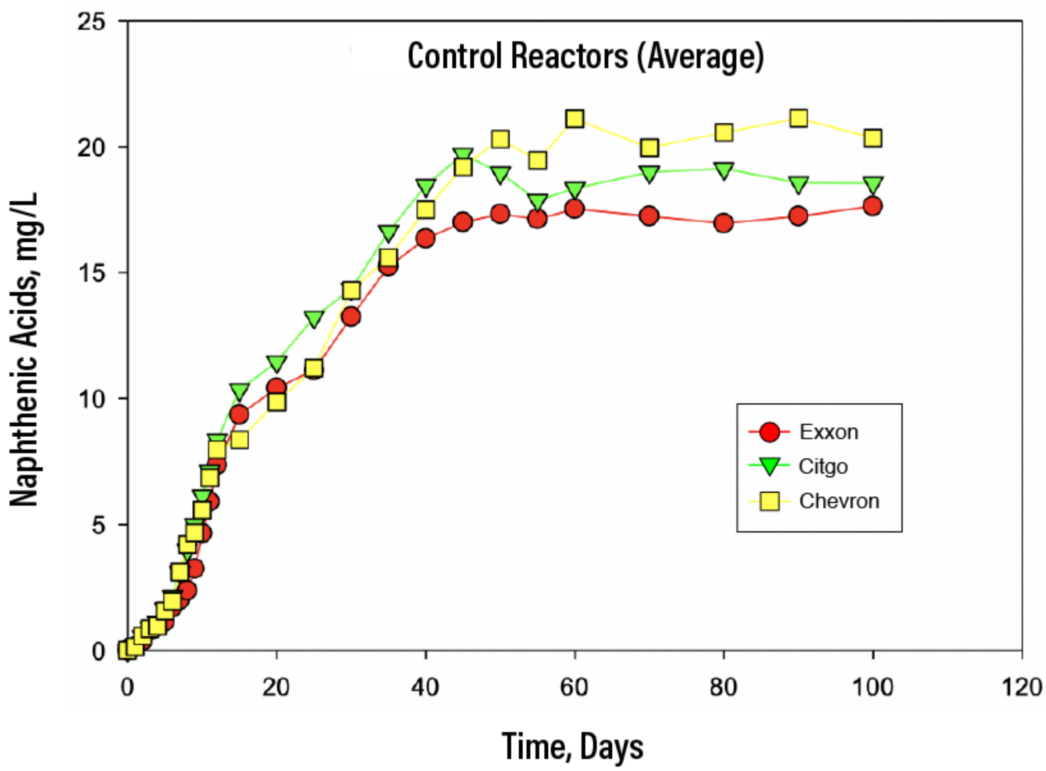


FIGURE 21. Naphthenic Acid Concentration in Control Activated Sludge Reactors Receiving Refinery Wastewater

As shown in Figure 22, nitrification appears to have started in the control reactors during the first 10 days. However, the degree to which this occurred was very small. Most of the ammonia that was oxidized was present in the form of nitrite, which typically indicates a poor nitrification population. Almost no nitrate was measured at any time during the study.

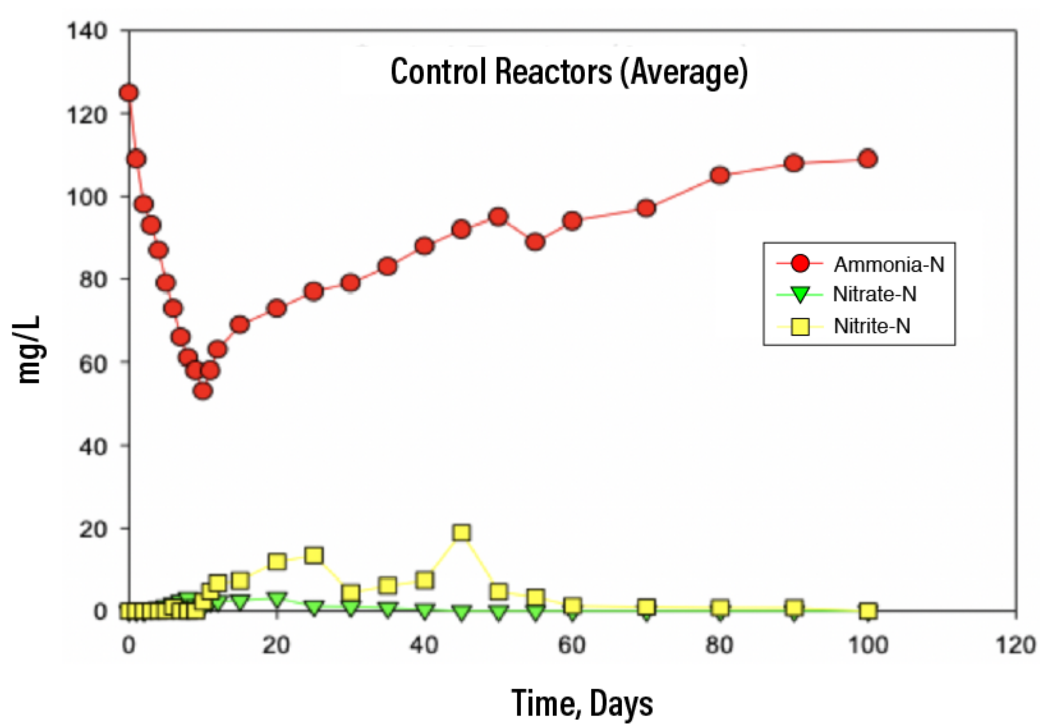


FIGURE 22. Ammonia-N, Nitrite-N and Nitrate-N Concentration in Control Activated Sludge Reactors Receiving Refinery Wastewater

The naphthenic acid concentration of the three processes with Kenaf are shown in Figure 23. There was some bioaccumulation evident in this reactor as well. Naphthenic acids increased from non-detectable to a maximum concentration of slightly more than five mg/L. This level was four times lower than measured in the control reactors, and was reproducible in the three Kenaf replicates. The level in the reactor contents was over two times lower than that in the influent, this indicates the biodegradation was able to overshadow bioaccumulation and that the degree of accumulation and inhibition would be much less. Concentrations of 5 ppm of naphthenic acids could still cause some degree of nitrification inhibition. However, the severity of this inhibition in the Kenaf reactors would likely be much less than for the control reactors.

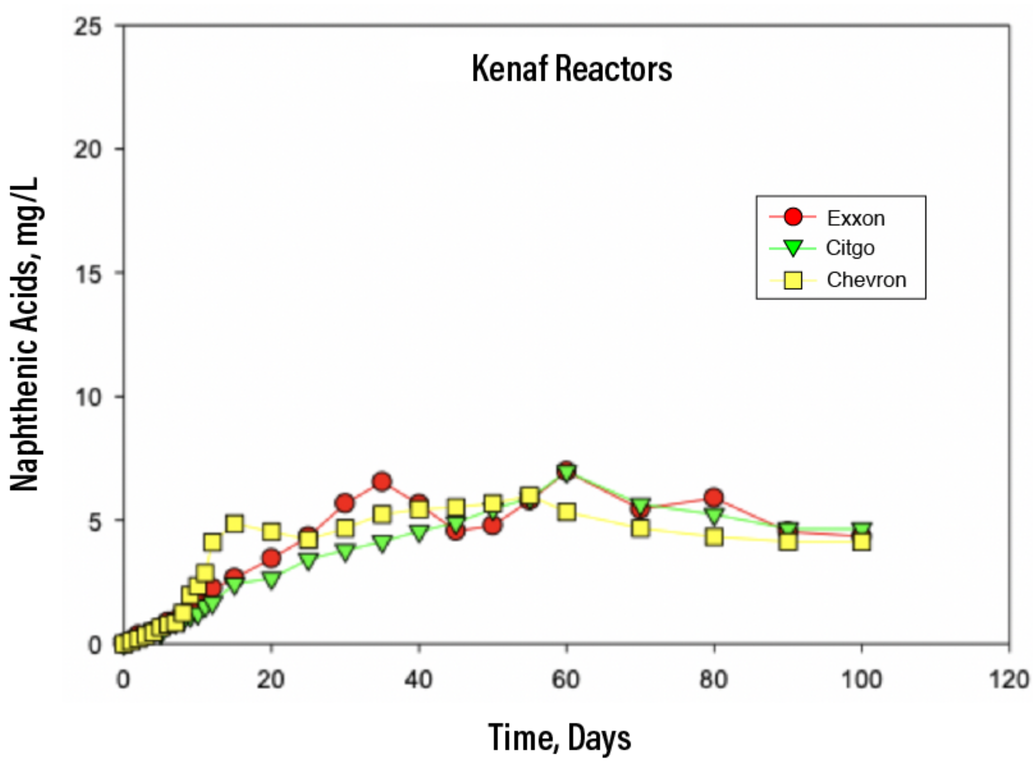


FIGURE 23. Naphthenic Acid Concentration in Kenaf Activated Sludge Reactors Receiving Refinery Wastewater

The ammonia concentration in the Kenaf reactors in Figure 24 was initially 127 mg/L. The ammonia concentration dropped, rather consistently over the first 10 days, and was below 10 mg/L after day 40. There was a significant spike in the nitrite nitrogen concentration after 10 days. The nitrite concentration decreased after this time and remained low thereafter. The nitrate nitrogen concentration increased rapidly over the first ten days and more slowly after this time. The maximum concentration of nitrate-N was 60 mg/L, which is much lower than the influent ammonia-nitrogen. This indicates that a significant amount of the nitrogen is not being nitrified, but is either being taken up as a nitrogen source or leaving the system via denitrification. Since the reactor contents had a dissolved oxygen in excess of 4.0 mg/L, denitrification in the bulk liquid is not likely.

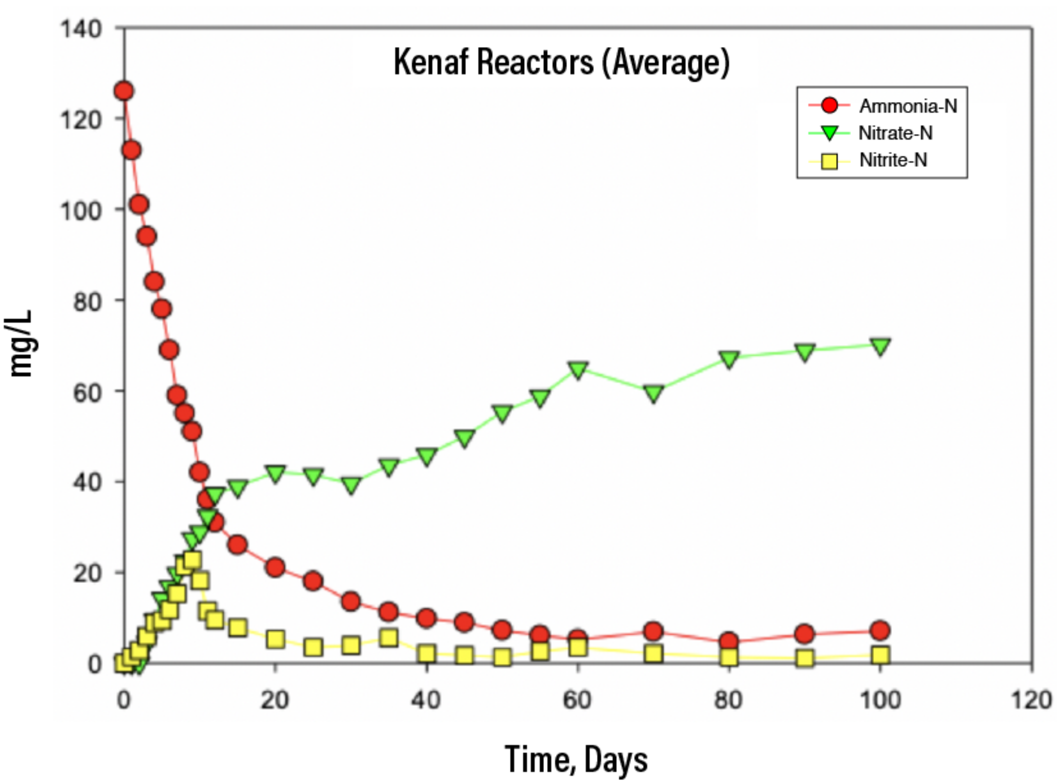


FIGURE 24. Ammonia-N, Nitrite-N and Nitrate-N Concentration in Kenaf Activated Sludge Reactors Receiving Refinery Wastewater

5) CONCLUSIONS

A study was conducted to assess the efficacy of Kenaf bio-media for improving activated sludge treatment of petroleum refinery wastewaters by reducing inhibition and providing a biological support medium. This study employed wastewater from three different refineries. Based on the results presented above, the following conclusions are made:

1) Kenaf has a good affinity for sorption of a number of inhibitory chemicals found in refinery wastewaters that pose problems for BOD removal and Nitrification processes. These chemicals include: phenols, o-cresol, p-cresol, aniline, benzene, toluene, and various alkanes.

2) The degree of sorption by Kenaf is only slightly lower than that achieved by many activated carbons currently utilized to help mitigate spills. Thus, Kenaf would be a viable alternative for use in the event of a minor spill and could help moderate the inhibitory effects on nitrification and BOD oxidation.

3) Soprtion by Kenaf is largely reversible. This means that the chemicals would be available for biodegradation. This could extend the life of the Kenaf in the process, making it even more attractive and cost effective.

4) The Kenaf has nearly neutral buoyancy when wet. This makes it superior to many carbons, whose density can cause problems with keeping it in suspension. Furthermore, since the density is similar to biomass, the apparent density of the particles will not change as biofilm grows.

5) The bacterial colonization of the Kenaf is relatively quick and high biomass densities can be attained. In testing, two times more biomass was present on colonized Kenaf than on a commercially available plastic support.

6) In activated sludges treating refinery wastewater, the Kenaf increased the rate and degree of BOD removal and individual inhibitory compound removal as well.

7) The Kenaf allowed more stable long-term BOD removal and lower effluent BOD concentrations.

8) Kenaf allowed Nitrification to occur to a much greater extent.

9) Kenaf allowed better biodegradation of naphthenic acids, likely by equalizing the concentrations seen by the biofilm. The decreased naphthenic acid concentration resulted in better nitrification performance.

10) There was evidence for some denitrification within the bioparticles. If this can be optimized, the process would become even more attractive for use in the refining industry.

Note: This paper is an excerpt from a large work made by Dr. Lange. The larger paper is available upon written request to Nuvoda.