

WRI-06-R006

FINAL REPORT

**APPLICATIONS OF LAYERED DOUBLE HYDROXIDES IN
REMOVING OXYANIONS FROM OIL REFINING AND COAL
MINING WASTEWATER**

**Base Task 2.e Topical Final Report
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ABSTRACT

Western Research Institute (WRI), in conjunction with the U.S. Department of Energy (DOE), conducted a study of using the layered double hydroxides (LDH) as filter material to remove microorganisms, large biological molecules, certain anions and toxic oxyanions from various waste streams, including wastewater from refineries. Results demonstrate that LDH has a high adsorbing capability to those compounds with negative surface charge. Constituents studied include model bacteria, viruses, arsenic, selenium, vanadium, diesel range hydrocarbons, methyl tert-butyl ether (MTBE), mixed petroleum constituents, humic materials and anions.

This project also attempted to modify the physical structure of LDH for the application as a filtration material. Flow characterizations of the modified LDH materials were also investigated. Results to date indicate that LDH is a cost-effective new material to be used for wastewater treatment, especially for the treatment of anions and oxyanions.

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EXECUTIVE SUMMARY

Wastewater generated from industries such as oil refining, coal mining, and CBM production, potentially contain high concentrations of toxic oxyanions. Current filtration materials have low loading capacities and are effective for only organic and metal cation removal. Due to their large surface areas and anion exchange capacities, layered double hydroxides (LDHs) have been demonstrated to be high potential materials for removing toxic arsenic and selenium oxyanions from wastewater streams.

Western Research Institute (WRI), in conjunction with the U.S. Department of Energy (DOE), conducted a laboratory-scale investigation of the feasibility of using LDH as filter material that removes toxic oxyanions from industrial wastewaters. The LDH material was synthesized in the laboratory and was tested in removing arsenic and selenium oxyanions from refinery wastewater. A side experiment was conducted, to investigate the potential of using LDH-lignin mixtures in removing sodium from CBM water. Other tests investigating continuous flow capacities of filters containing LDH as the primary filter material. The results of the tests indicated the following:

- LDH does remove arsenic, selenium and other oxyanions; however, efficiency is increased if water is pre-treated with activated carbon to remove any organics that may interfere with oxyanion adsorption by LDH.
- LDH-lignin mixtures do not remove sodium from CBM water. Increased sodium concentrations are observed, which is the result of sodium released from the LDH. Free sodium may be present in the material due to the excess sodium hydroxide that is used in the production of LDH.
- Filters with LDH as the primary filter material are not feasible. LDH expands in the presence of water, which results in the eventual loss of flow through the filter. Granulating LDH with cement increased LDH stability in water; however, the LDH eventually expanded and flow through the filter was significantly decreased.

In summary, LDH is an attractive material in removing toxic anions from industrial wastewaters; however, overcoming LDH expanding properties is a challenge in developing a filtration device with LDH as the primary filter material. Possible mixing of LDH with other materials may overcome this challenge.

BACKGROUND

Layered double hydroxides (LDHs) are materials with unique layered structures. The general formula of LDHs is $[M^{2+}_{1-x}M^{3+}_{1-x}(\text{OH})_2]^{x+}X^{m-} \cdot n\text{H}_2\text{O}$, where M^{2+} and M^{3+} are bivalent and trivalent cations, respectively, in octahedral positions and X^- is an anion positioned between interlayer. LDHs are rare in nature, but can be synthesized by co-precipitating bivalent and trivalent metal salts with a base under controlled conditions (Miyata, 1975, 1980; Rhee et al., 1997). Our group has successfully synthesized various types of LDHs (e.g., Mg-Al-Cl, Zn-Al-Cl, Fe-Al-Cl), and initial data show good results of removing biological agents (e.g., bacteria, viruses), which have negative surface charge, from aqueous and air phases.

Oxyanions such as arsenic (As) and selenium (Se) are a group of toxic constituents in wastewater generated from industries such as refining, coal mining, and coal bed methane (CBM) production. As and Se oxyanions in land drainage waters have been reported to adsorb to LDHs due to their high anion exchange capacities and surface area (Miyata, 1980, 1983; You et al., 2001a, 2001b), which make LDHs a potential material for removing these toxins from industrial wastewater sources. Existing filtration materials include activated carbon, ion exchange resins, and synthetic fabrics. Filtration systems using these sorbents are effective in the removal of organic compounds and certain cationic metals such as lead and mercury. The loading capacities of these materials are usually low and frequent filter changes are necessary. Most of these sorbents possess negatively charged surfaces; therefore fail to adsorb negatively charged oxyanions and cyanides. Organic substances can be intercalated with LDH (You et al., 2002) and cations, such as sodium, may also be removed by combining LDH with lignin, where lignin provides an anionic surface. Reverse osmosis (RO), which uses nano-membranes as the filters, is a highly effective tool to eliminate all impurities from water; however, the high cost of this technology prohibits its use in industrial wastewater treatment. The unique positive charge of LDHs and its selective affinity to oxyanions demonstrates a promising technology of removing Se and As from wastewater streams in various industries.

WRI in conjunction with the U.S. DOE, under Task 2.e, conducted a laboratory-scale investigation of the feasibility of using LDHs in removing As, Se and other constituents of concern (COC) from industrial wastewaters. The goal of this project was to develop an innovative filtration device/process that uses LDH as the main filtration material to cost-effectively remove arsenic, selenium and other COC from different sources of industrial wastewater.

RESULTS AND DISCUSSION

LDH Synthesis

Mg-Al, (Mg/Al = 2), and Zn-Al (Zn/Al = 2) LDHs were prepared by following and modifying the method described in Miyata 1975, 1980. AgNO₃ solution was used to determine if LDH was free of Cl⁻. One kilogram of LDH-Mg/Al and LDH-Zn/Al were synthesized for further tests. The obtained LDH has the size of 0.1 mm to 0.5 mm diameter. LDH was crushed to proper sizes when different tests are conducted.

CBM Water Sodium Adsorption Column Study

The CBM water collected from a site in northern Wyoming (Cooksley 1-15 Boxelder). Background concentration of sodium (Na⁺) was analyzed by atomic absorption (AA) spectroscopy (Department of Geology and Geophysics, University of Wyoming). 5 g of Mg-Al LDH, 5 g organosolv lignin, and 5 g alkali lignin were used in setting up the column studies (20-ml syringes were used for the columns). Reverse osmosis water was used as controls of each treatment described in Table 1. Na⁺ concentrations were analyzed by AA spectroscopy.

Table 1. Treatments for Na⁺ adsorption study

Sample ID	Description	Sample Collected
CBM1	CBM water background	
RO1	RO water background	
CBM2a	organosolv lignin filled column	at beginning
CBM2b	organosolv lignin filled column	100 ml
CBM2C	organosolv lignin filled column	200 ml
RO2a	organosolv lignin filled column	at beginning
RO2b	organosolv lignin filled column	100 ml
RO2c	organosolv lignin filled column	200 ml
CBM3a	alkali lignin filled column	at beginning
CBM3b	alkali lignin filled column	100 ml
CBM3c	alkali lignin filled column	200 ml
RO3a	alkali lignin filled column	at beginning
RO3b	alkali lignin filled column	100 ml
RO3c	alkali lignin filled column	200 ml
CBM4a	Mg-Al LDH filled column	at beginning
CBM4b	Mg-Al LDH filled column	100 ml
CBM4c	Mg-Al LDH filled column	200 ml
RO4a	Mg-Al LDH filled column	at beginning
RO4b	Mg-Al LDH filled column	100 ml
RO4c	Mg-Al LDH filled column	200 ml
CBM5a	organosolv-alkali-LDH column	at beginning
CBM5b	organosolv-alkali-LDH column	100 ml

CBM5c	organosolv-alkali-LDH column	200 ml
RO5a	organosolv-alkali-LDH column	at beginning
RO5b	organosolv-alkali-LDH column	100 ml
RO5c	organosolv-alkali-LDH column	200 ml
CBM6a	alkali-organosolv-LDH column	at beginning
CBM6b	alkali-organosolv-LDH column	100 ml
CBM6c	alkali-organosolv-LDH column	200 ml
RO6a	alkali-organosolv-LDH column	at beginning
RO6b	alkali-organosolv-LDH column	100 ml
RO6c	alkali-organosolv-LDH column	200 ml

Results for sodium adsorption study are shown in Table 2. The results suggest that LDH is not a feasible method of removing sodium from CBM water. The concentration of sodium in the CBM water collected at the outlet of the LDH column either did not change significantly or actually increased. The RO water column tests show increased concentration of sodium at the column outlet. This suggests that LDH may contain free sodium, possibly from excess sodium hydroxide used during co-precipitation.

Table 2. Results for Na⁺ adsorption study

ID	ppm Na
CBM1	417.0
RO1	1.0
CBM2A	409.7
RO2A	7.6
CBM2B	400.0
RO2B	1.4
CBM2C	389.2
RO2C	0.6
CBM3A	857.5
RO3A	372.4
CBM3B	426.5
RO3B	71.2
CBM3C	437.0
RO3C	36.4
CBM4A	2756.6
RO4A	3568.8
CBM4B	460.1
RO4B	106.7
CBM4C	433.8
RO4C	96.0

CBM5A	3047.7
RO5A	4266.5
CBM5B	422.7
RO5B	252.0
CBM5C	407.2
RO5C	57.0
CBM6A	5271.4
RO6A	5213.7
CBM6B	534.0
RO6B	461.1
CBM6C	413.6
RO6C	255.9

Refinery Wastewater As and Se Adsorption

Water from a wastewater stream was collected from Frontier Refinery (Cheyenne, WY). The concentrations of As and Se were determined by ICP-MS (Department of Geology and Geophysics, University of Wyoming) to be 27.3 ppm and 322.7 ppm, respectively. LDH (Mg/Al = 2) was suspended at various amounts in 25 ml of refinery wastewater. The suspensions were shaken and samples were collected after 15, 30, 60, 120 and 180 minutes. Results are shown in Figures 1 and 2.

Figure 1 shows the percent drop in As after LDH treatment, which ranged from 34 to 49%. A 58 to 79 % drop in Se was the general trend as shown in Figure 2. The drop in As and Se did not change significantly throughout 180 minutes.

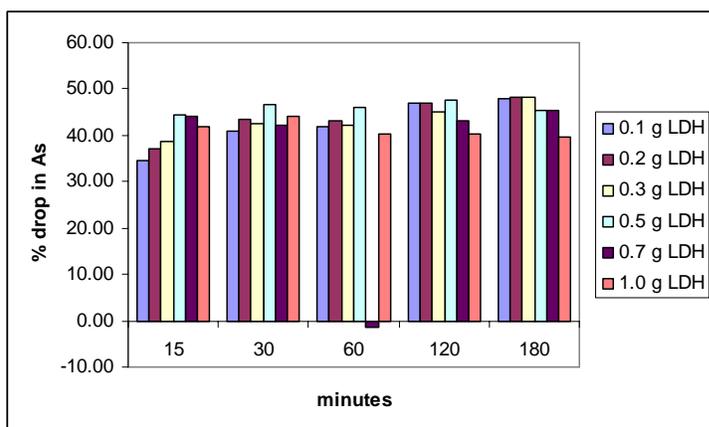


Figure 1. As Removal in LDH Suspension Treatment

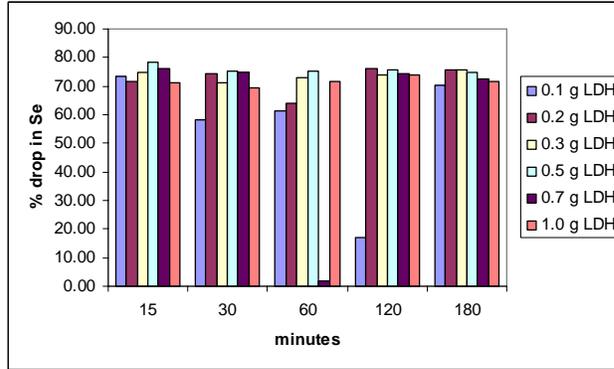


Figure 2. Se Removal in LDH Suspension Treatment

Activated carbon was used in the following study to determine the amount of organics that could be removed from the refinery water, which may enhance the performance of the LDH in removing oxyanions. 12.0 g of carbon was added to 200 ml of refinery wastewater (0.06 g/ml) in a centrifuge tube. The carbon suspension was shaken for 30 minutes. The supernatant was analyzed for the following parameters:

1. Arsenic
2. Selenium
3. Vanadium
4. Chromium
5. Lead
6. Gasoline Range Organics (GRO)
7. Diesel Range Organics (DRO)
8. Volatile Organic Compounds (VOC)
9. Fluoride
10. Chloride
11. Bromide
12. Nitrate
13. Phosphate
14. Sulfate

Where the metals/metal oxyanions were determined by ICP-MS, DRO was determined by GC-FID, GRO was determined by SW8015M as G, and VOCs were determined by SW8260B.

Mg-Al LDH was crushed into fine powder and mixed in 200 ml of refinery wastewater in amounts of 2.4, 5.6, and 12.0 g (0.012, 0.028, and 0.060 g/ml, respectively). The suspensions were shaken for 5, 15 and 30 minutes. The supernatant were collected and analyzed for the same parameters as the carbon treatment supernatant. The analyses results for anions and metals/metal oxyanions are shown in Table 3 below.

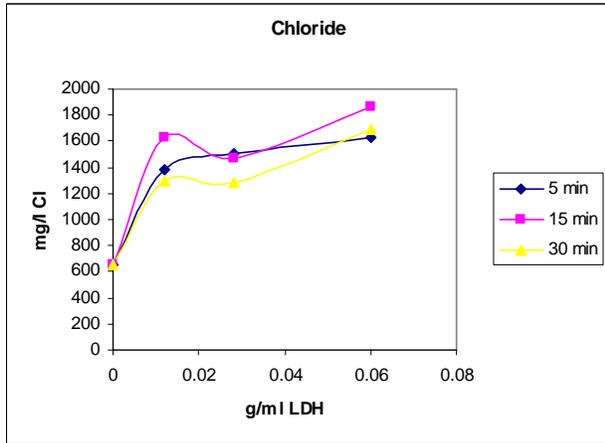
Table 3. Tabulated Analysis Results for LDH and Carbon Suspension Study

		mg/L					
Treatment		F ⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
Refinery	Water						
Background		42.47	653.76	ND	ND	26.688	122.601
0.06 g/ml Carbon	30 min	36.59	825.22	ND	ND	13.288	150.148
0.012 g/ml LDH	5 min	2.6	1384.46	3.131	ND	33.752	37.194
0.028 g/ml LDH	5 min	ND	1501.12	2.98	ND	30.851	14.721
0.060 g/ml LDH	5 min	ND	1633.44	ND	ND	26.137	3.771
0.012 g/ml LDH	15 min	0.19	1627.52	2.967	ND	33.122	14.633
0.028 g/ml LDH	15 min	2.28	1465.3	3.056	ND	30.981	6.473
0.060 g/ml LDH	15 min	ND	1858.68	ND	ND	30.363	4.111
0.012 g/ml LDH	30 min	ND	1296.34	ND	ND	29.227	10.302
0.028 g/ml LDH	30 min	ND	1283.76	ND	ND	30.736	6.34
0.060 g/ml LDH	30 min	7	1688.16	ND	ND	24.85	3.479

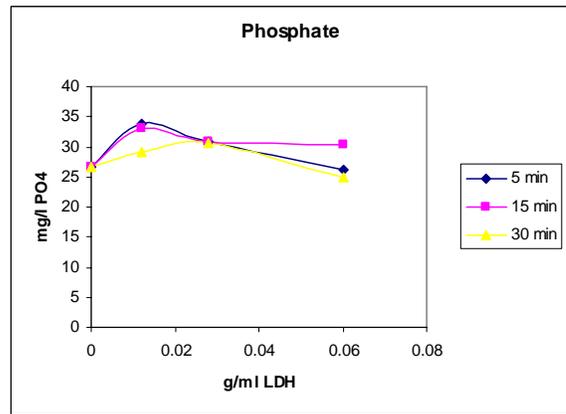
Table 3. Tabulated Analysis Results for LDH and Carbon Suspension Study (cont'd)

		ppb				
Treatment		V	Cr	As	Se	Pb
Refinery	Water					
Background		22.0	16.7	39.7	301.3	1.0
0.06 g/ml Carbon	30 min	22.6	28.2	28.0	76.3	1.6
0.012 g/ml LDH	5 min	18.8	7.6	16.4	215.2	1.0
0.028 g/ml LDH	5 min	18.7	7.2	13.8	196.5	1.0
0.060 g/ml LDH	5 min	23.4	6.8	15.7	175.8	1.1
0.012 g/ml LDH	15 min	18.4	6.8	21.6	277.1	1.0
0.028 g/ml LDH	15 min	19.0	7.0	15.4	193.3	1.0
0.060 g/ml LDH	15 min	24.2	6.8	15.9	161.4	0.7
0.012 g/ml LDH	30 min	17.5	6.4	19.9	258.1	1.2
0.028 g/ml LDH	30 min	18.0	7.8	14.7	191.1	1.2
0.060 g/ml LDH	30 min	22.4	6.1	12.5	162.1	1.0

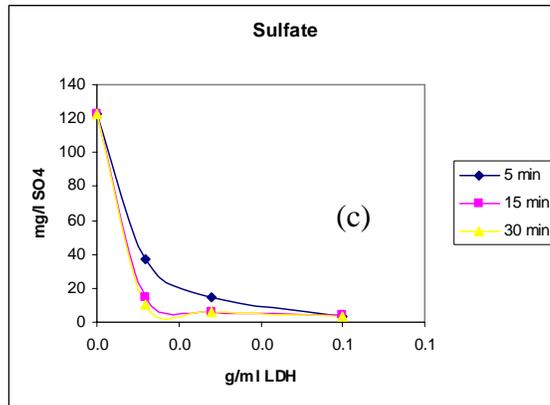
Figure 3 shows the effect of LDH concentration in removing chloride (a), phosphate (b), and sulfate (c), for shaking period. The amount of chloride increased with increasing amount of LDH, which suggests incomplete removal of chloride during cleaning step in LDH synthesis. LDH is shown to have little or no effect in removing phosphate; however, there is significant removal of sulfate with 88-97% efficiency for the treatments that were shaken for 15 and 30 minutes (91 % for 0.06 g/ml LDH after 5 minutes).



(a)



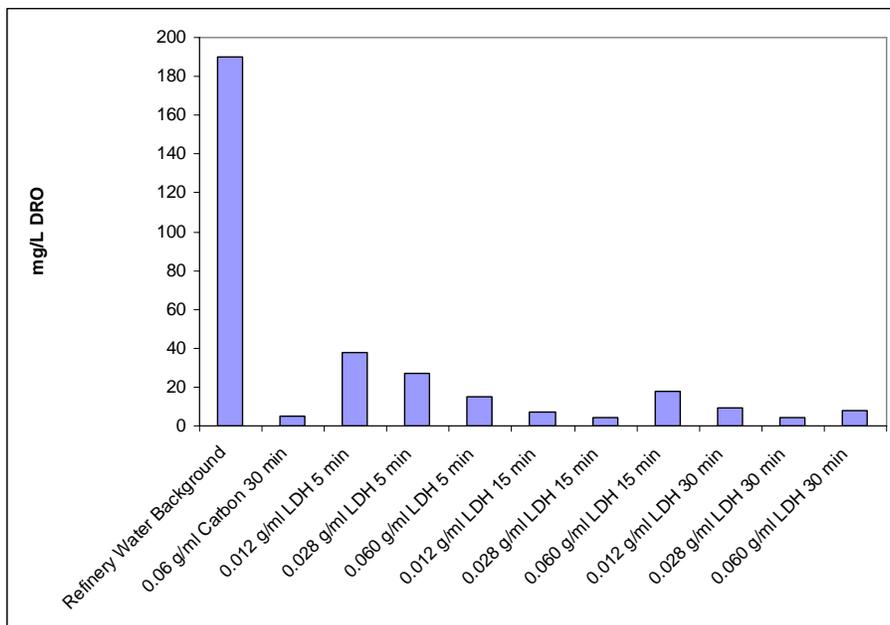
(b)



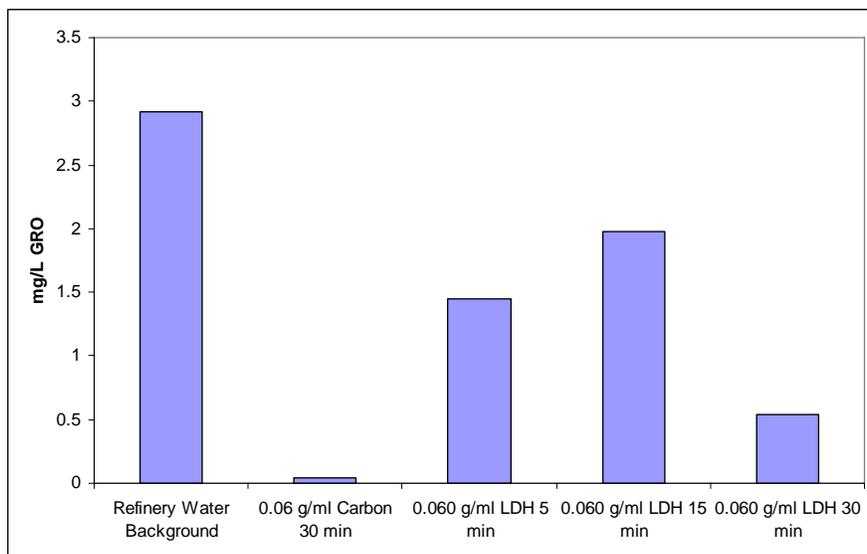
(c)

Figure 3. Effect of LDH Amount on Removal of Anions

Figure 4 shows effects of carbon, LDH concentration, and mixing times, on the removal of DRO and GRO. The carbon removed 98% of DRO, and the LDH removed 80-98% of the DRO from the refinery wastewater. This indicates possible interference in the LDH's performance in removing toxic metal oxyanions from the wastewater. The carbon removed 99% of the GRO, and 0.060 g/ml LDH removed 32-47% of the GRO while shaken up to 15 minutes. A 82% removal of GRO was observed for LDH after 30 minutes.



(a)



(b)

Figure 4. Results for DRO and GRO Removal

Carbon removed 97-100% of all VOCs in the wastewater (Figure 5). The LDH removed 65-87% of all the VOCs (Figure 3), except for 2-butanone. The removal of organics by LDH indicates interference with its performance in removing toxic metal oxyanions from refinery wastewater may occur. Pre-treating the wastewater with carbon may eliminate the majority of this interference.

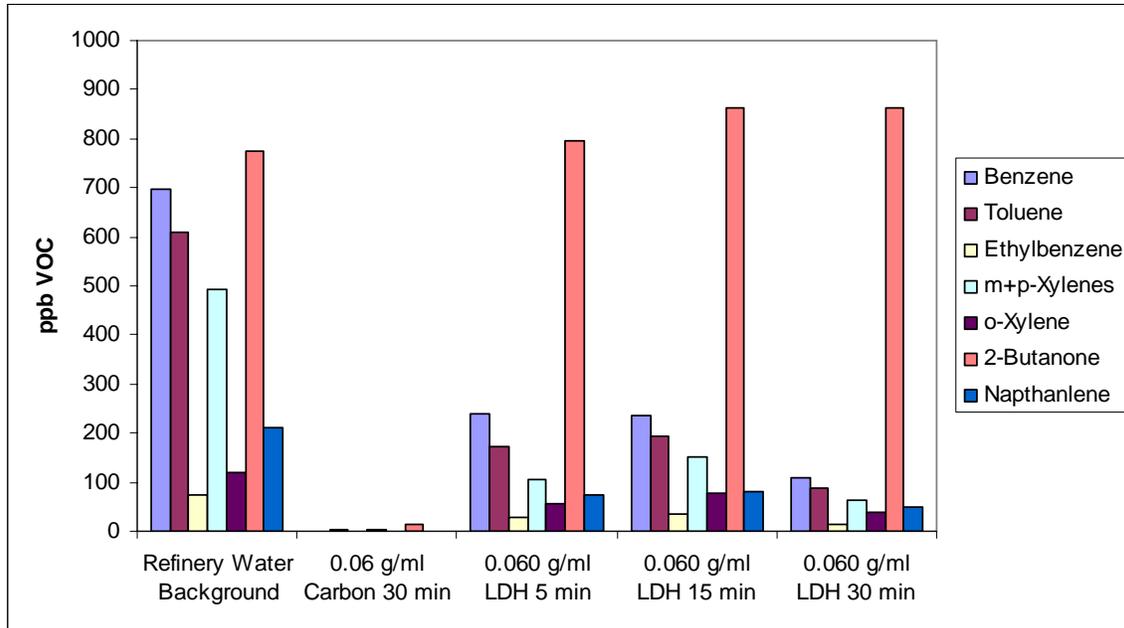


Figure 5. Results for VOC Removal

Figure 6 shows the amount of As and Se oxyanions that were removed at various concentrations of LDH and mixing times. The amount of As removed was up to 69% and the amount of Se removed was up to 46%.

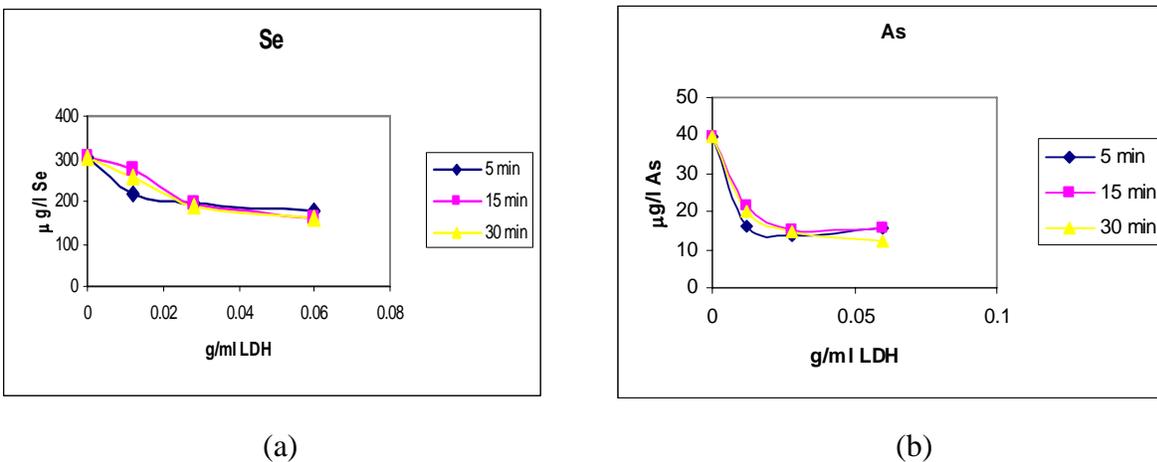


Figure 6. Results for As and Selenium Removal

The following tests were treated with carbon to remove most of the organics in the refinery wastewater, and tests to determine the effects of LDH amounts and mixing times were conducted afterwards. 12.0 g of carbon was added to each of nine centrifuge tubes containing 200 ml of refinery wastewater, and the mixtures were shaken for 30 minutes. The tubes were centrifuged and the supernatant were treated with 2.4, 5.6 and 12.0 g LDH. The treatments were shaken for 5, 15 and 30 minutes. The supernatant were analyzed for DRO, As, Se, V, and Pb.

0.01 g LDH / ml removed 13.1 % of the As from the refinery water (Figure 7). 51.8% of

the As was removed by 0.03 g LDH / ml, and 54.3% was removed by 0.06 g LDH / ml.

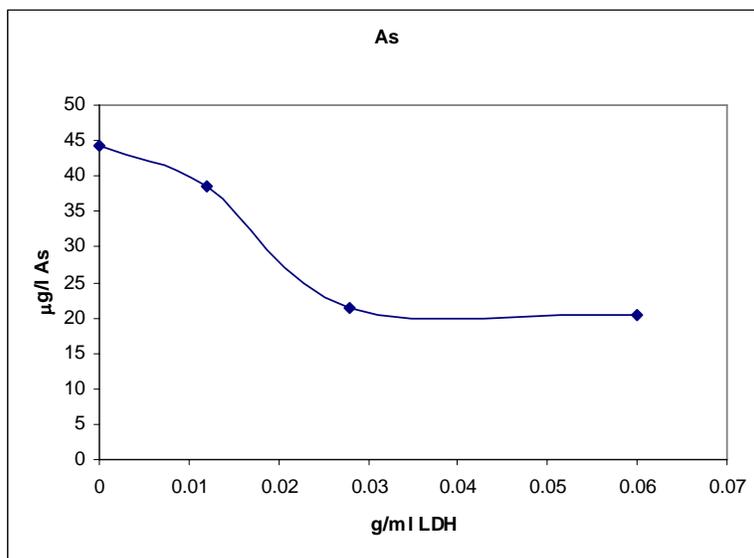


Figure 7. As Removal from Refinery Wastewater

The removal of Se from the refinery water is illustrated in Figure 8. 0.01 g LDH / ml removed 32.7% of the Se, 0.03 g LDH / ml removed 64.4 %, and 0.06 g LDH / ml removed 66.6% of the Se.

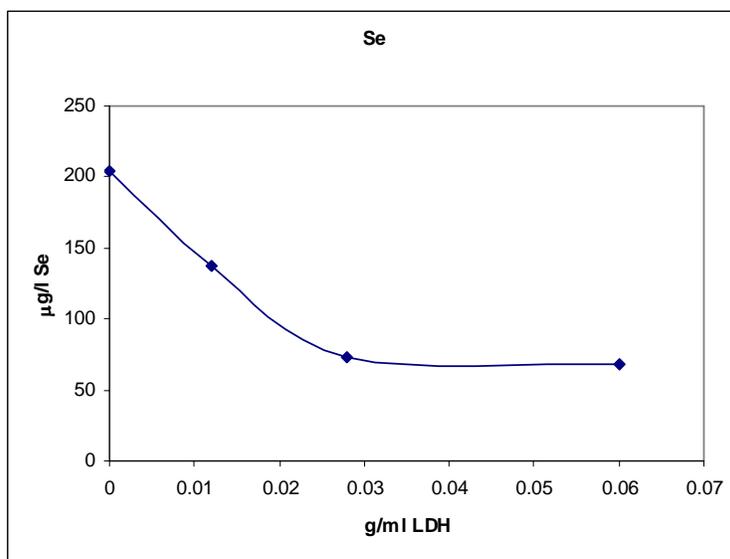


Figure 8. Se Removal from Refinery Wastewater

LDH removed up to 34.3 % of the V from the refinery water (Figure 9), but up to 85.7% removal of Pb was observed for 0.06 g LDH / ml (Figure 10). No DRO was detected for each treatment, indicating removal by activated carbon. Removal of As, Se, V, and Pb from the refinery water increased which indicates carbon pretreatment reduced the interference caused by the organic contaminants.

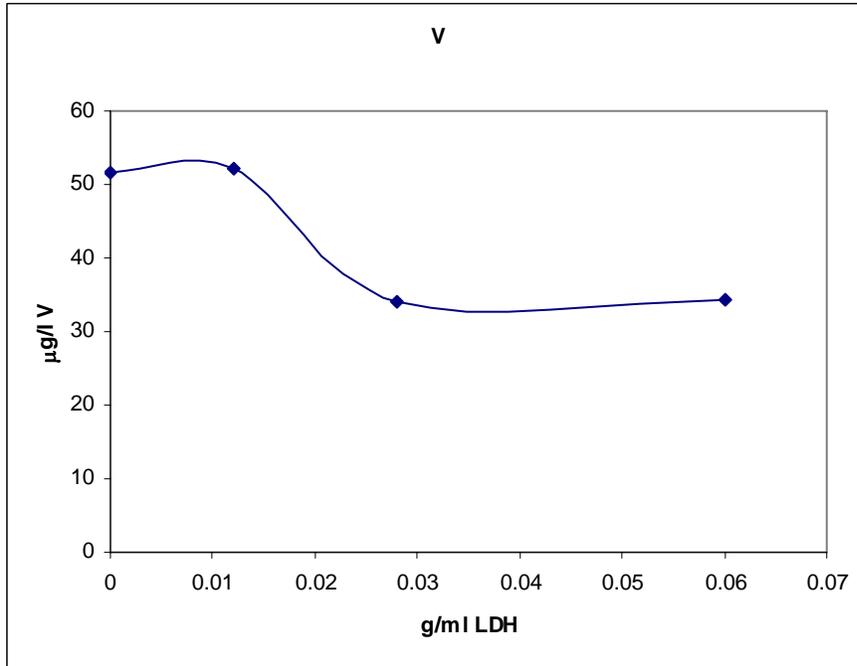


Figure 9. V Removal from Refinery Wastewater

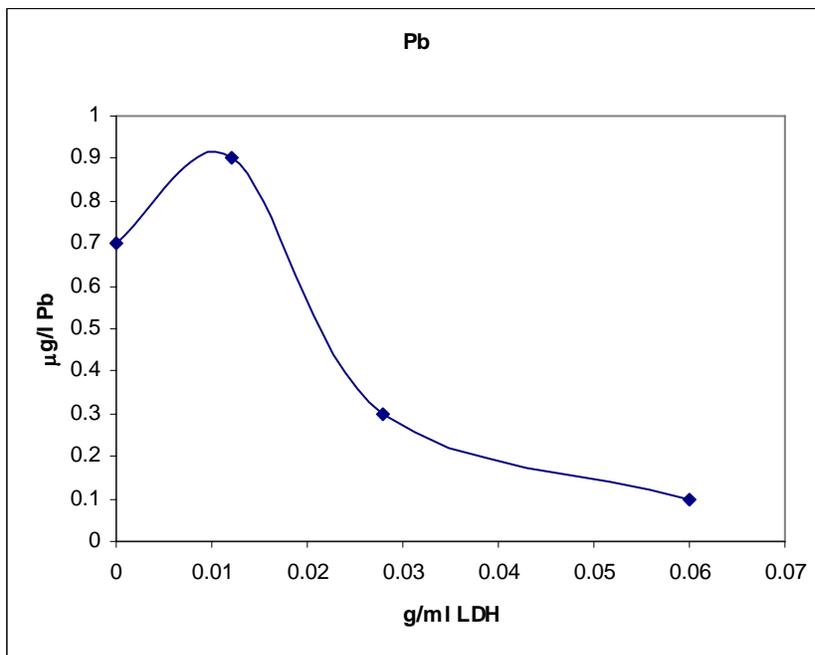


Figure 10. Pb Removal from Refinery Wastewater

Tests that involved LDH “bags” were conducted in the same fashion as the suspension tests. 2.4, 5.6, and 12.0 g LDH were wrapped in cheesecloth and stirred in refinery wastewater for 5, 15 and 30 minutes. The carbon was in suspension only.

Carbon removed 70 to 100 % of the VOCs and 98.7% of the DRO from the refinery water (Figures 11 and 12). 0.06 g LDH / ml removed up to 50.8 to 84.0 % of the VOCs and 72.2 to 89.5% of the DRO.

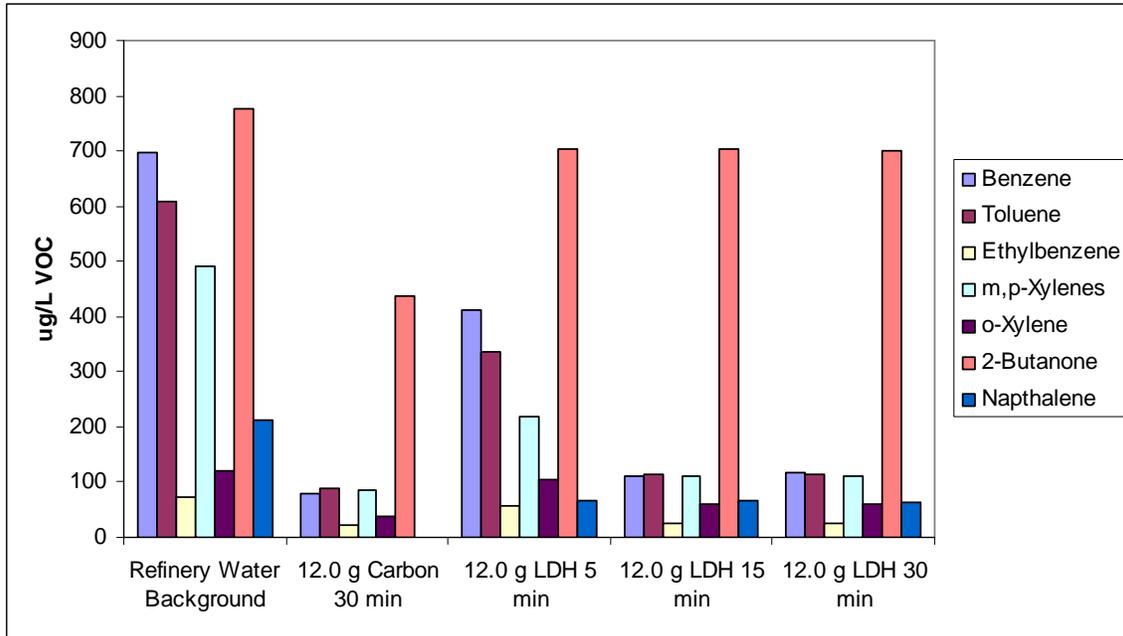


Figure 11. VOC Removal from Refinery Wastewater

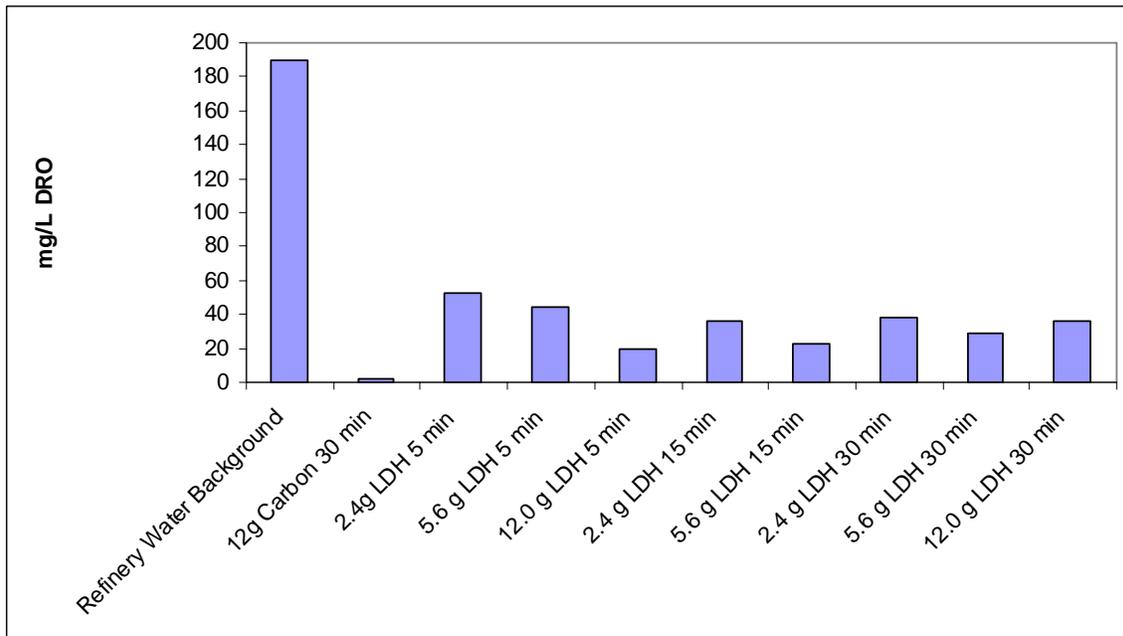


Figure 12. DRO Removal from Refinery Wastewater

Figures 13, 14 and 15, show that anions are being released from the LDH bags. These anions may be from the bag material itself and increased competition by anions and oxyanions due to decreased LDH contact area may be responsible for the lack of anion uptake by the LDH.

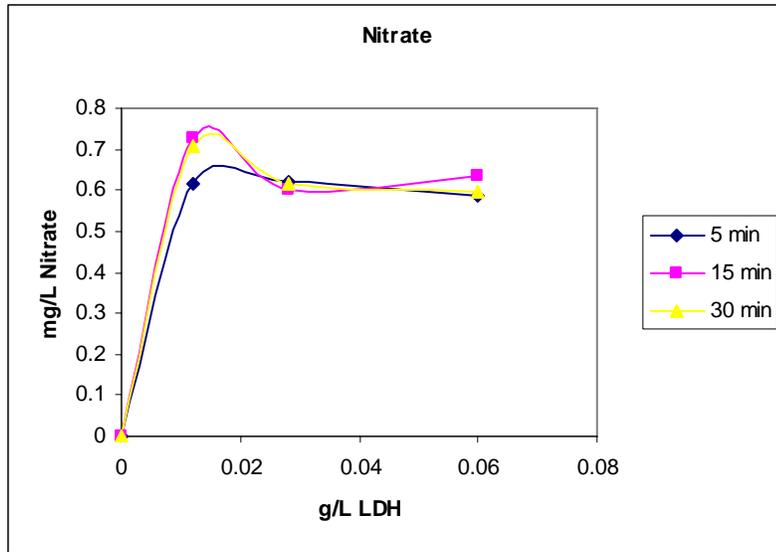


Figure 13. Nitrate Release from LDH Bag

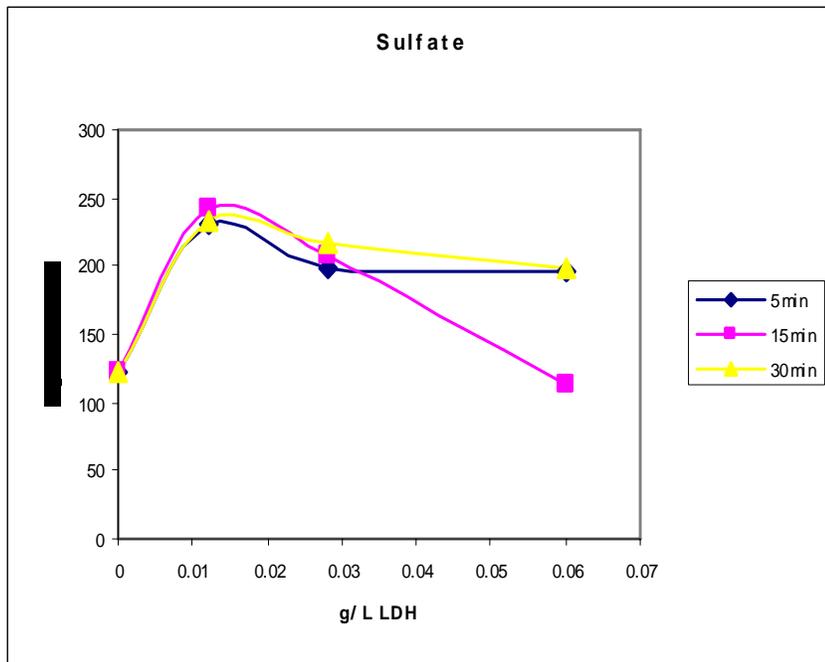


Figure 14. Sulfate Release from LDH Bag

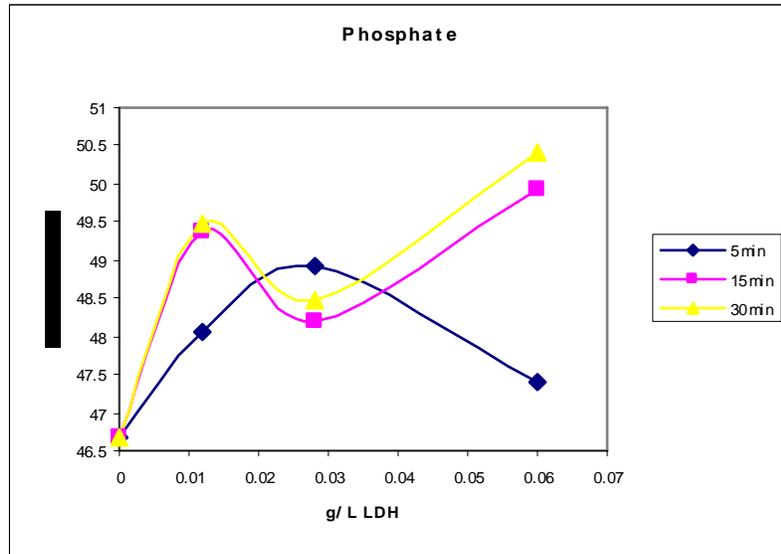


Figure 15. Phosphate Release from LDH Bag

All of the As was removed by LDH within 5 minutes of agitation by the LDH-bag (Figure 16). However, As appears to have been released after 5 minutes and no re-uptake of As was observed. Only up to 23.7% of Se was removed by the LDH-bag (Figure 17).

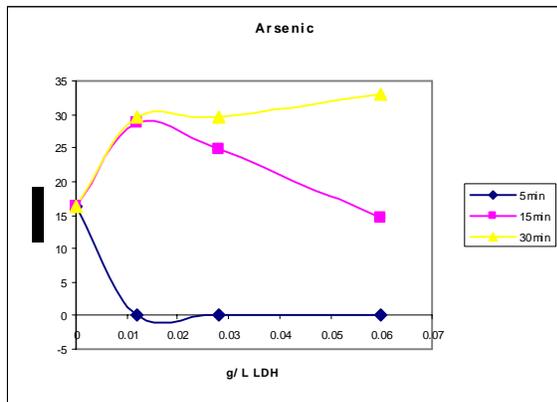


Figure 16. As Removal by LDH Bag

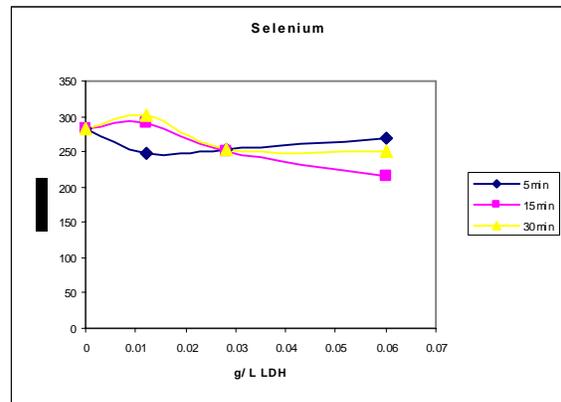


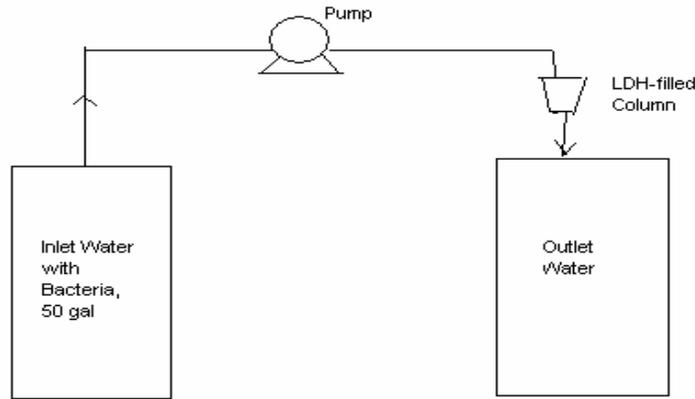
Figure 17. Se Removal by LDH Bag

Continuous Flow Study

Column studies with long periods of continuous flow of water were conducted using Mg-Al LDH (Mg/Al = 2). This test is to determine the maximum loading capacity and the instantaneous affinity of LDH to bacteria. Approximately 100 ml of raw river water (Laramie River) was added to tap water in a 50-gal drum this dilution was based on preliminary bacterial enumeration. 40 g of LDH was added to the column. A diagram of the apparatus design is shown in Figure 18. An initial flow rate of 500 ml/min was obtained by using existing LDH

material. However, LDH was powdered when hydrated during the preliminary column test, due to the plugging of pores in the column. Process modifications are undergoing to stabilize the granular LDH formation and sustain a continuous flow in the testing columns.

Figure 18. Continuous flow study apparatus



The purpose of this experiment was to determine the best possible ratio of LDH to Portland Cement (PC) to Water. Prior combinations resulted in flow that was either too high or too low. All trials were performed using the same LDH batch (#LB-05), PC and Water. The LDH was first measured out for each sample to 3.0 g. Next, the LDH and weighing cup were brought to tare and different percentages of LDH added. Three samples were created for each percentage of PC. The LDH and PC were then thoroughly mixed and water was then added using a syringe. Water was added into the first sample of each PC percentage mixtures until they reached a medium consistency. In the remaining two samples of each PC percentage mixtures were added + and - 0.2 ml to obtain an under and over saturated sample. The mixtures were then compacted using a hammer and bolt that matched the diameter of the weighing cup and allowed to dry for 24 hours. Each sample was then analyzed for a suitable flow. This was based on visual observations (i.e. too fine or too coarse results). Results are shown in Table 4 below.

Table 4. Tabulated Results for LDH:Cement:Water Ratios

Sample	Amount H ₂ O for undersat. consistency	Result	Amount H ₂ O for medium consistency	Result
90% LDH & 10% PC	0.267 mL/g	Very Fine	0.333 mL/g	Fine
85% LDH & 15% PC	0.167 mL/g	Fine	0.233 mL/g	Fine
83% LDH & 17% PC	0.167 mL/g	Fine	0.233 mL/g	Fine
80% LDH & 20% PC	0.267 mL/g	Coarse	0.333 mL/g	Coarse

Sample	Amount H₂O for saturated consistency	Result		
90% LDH & 10% PC	0.400 mL/g	Very Fine		
85% LDH & 15% PC	0.300 mL/g	Fine		
83% LDH & 17% PC	0.300 mL/g	Fine		
80% LDH & 20% PC	0.400 mL/g	Coarse		

The amount of water had little/no bearing on resulting textures, with the exception of the 10% LDH. No ideal LDH: PC: H₂O ratio, could be found. Results were either always too coarse or too fine. The line between coarse may be between 17% and 20% PC, however the textural differences between 10% and 17% were almost undetectable. This led to the assumption that the line between a fine and coarse textured result is between 17% and 20%.

Continuous flow studies involving LDH cement were conducted using the apparatus in Figure 18. Removal of bacteria in water was used as an indicator of LDH-cement quality. Three tests were conducted using 15 g and 10 g of LDH-cement (10% cement), and using a mixture of LDH-cement and pure LDH. The column that was filled with 15 g of LDH-cement (10% cement) had an initial water flow of 155 ml/min, which eventually dropped to 5 ml/min. The column with 10 g of LDH-cement (10% cement) had an initial flow of 345 ml/min, but the flow decreased to 55 ml/min after one hour. A mixture of 4.7 g LDH-cement (10% cement) and 5.8 g pure LDH was added to the column. The initial water flow was 330 ml/min and decreased to 95 ml/min after one hour. Figure 19 shows the bacteria removal efficiency of each test. The LDH-cement and pure LDH mixture maintained the greatest removal efficiency at 80-82%.

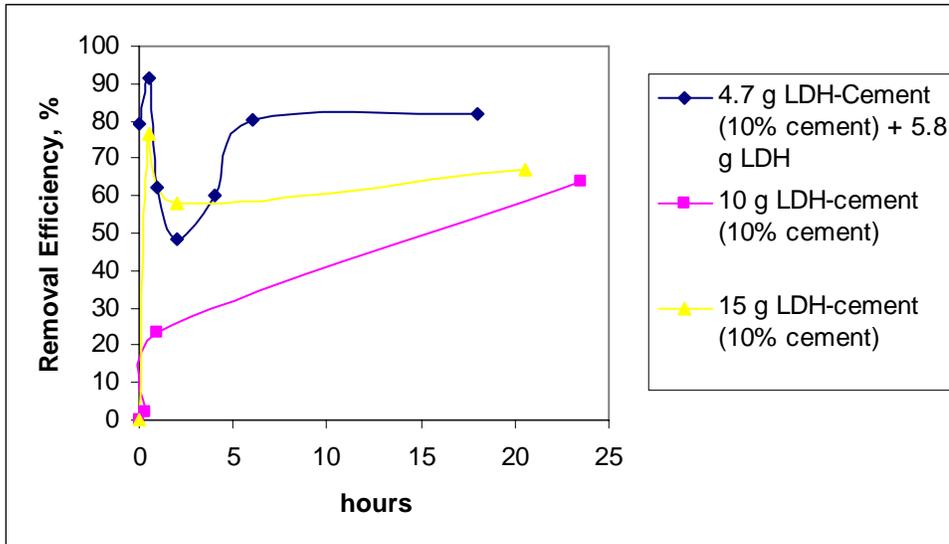


Figure 19. Bacteria Removal Efficiencies of LDH and LDH-Cement (10% Cement)

An additional continuous flow test was conducted where the column contained 10 g of LDH-cement (20% cement) and water flow was initially 269 ml/min. The flow decreased to 155 ml/min after 30 minutes, and then to 10 ml/min after 5 hours. This indicates LDH-cement (20% cement) was still too fine for proper water flow. Bacteria removal efficiency was determined to be 17.23%.

A capacity flow tests was conducted using two of the same apparatus shown in Figure 16. One column was filled with 2-mm LDH-cement (20% cement) particles and the other column was filled with 1.7-mm LDH-cement (20% cement) particles. For the 2-mm particles, the initial flow was 880 ml/min, but decreased significantly to 335 ml/min after 180 min (Figure 20). The flow leveled out at 210 to 260 ml/min. For the 1.7-mm particles, the initial flow was 830 ml/min, but decreased to 150 ml/min after 360 min. The flow leveled at 140 to 150 ml/min.

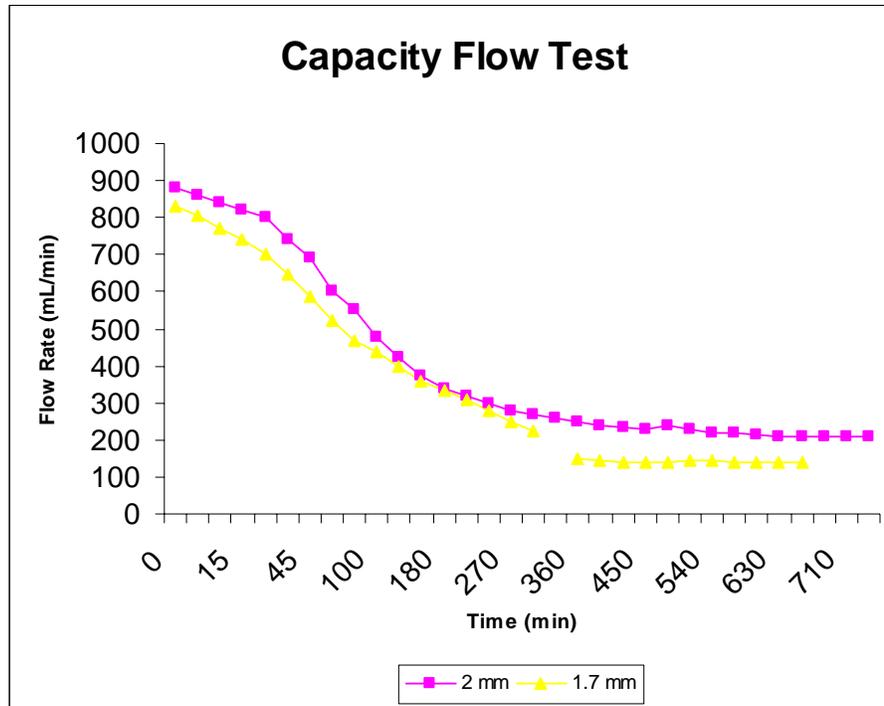


Figure 20. LDH Material Flow Test

Based on continuous flow tests, development of a filtration device is a major challenge. LDH has a structure that expands in the presence of water, which results in clogging of pores. Granulation of LDH with cement does increase the structural stability of the filter material; however, eventual expansion of LDH occurs. A possible alternative that may be investigated would be the mixing of activated carbon and LDH.

SIGNIFICANCE

Western Research Institute (WRI), in conjunction with the U.S. Department of Energy (DOE), conducted a laboratory-scale investigation of the feasibility of using LDH as filter material that removes toxic oxyanions from industrial wastewaters.

There is significant potential for using LDH to remove toxic oxyanions from industrial wastewaters. LDH was demonstrated to effectively remove As and Se from refinery wastewater. However, flow is lost through filters that contain LDH as the primary filter material. The results of this project indicate that LDH cannot be the primary filter material; however, it may be possible to mix LDH with a co-material (possibly activated carbon) in order to maintain continuous flow through a filtration device designed to remove toxic oxyanions from industrial wastewaters.

Two patents have been filed with the United States Patent Office for the applications of LDH to remove constituents of concerns from both air and liquid phases.

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