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REMOVAL HEAVY METALS FROM WATER WITH CNM

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Abstract - Heavy metals (HM) are described as metallic elements that have a moderately high density associated to water. With the statement that heaviness and toxicity are inter-related, heavy metals also contain metalloids, such as arsenic (As), that are able to produce toxicity at low level of publicity. The most common heavy metals are copper and lead, which can be very lethal to health and the surrounding environment as well. In order to get clean and safe water, these toxic chemicals must be removed. the research aims to removal three heavy metals (Cadmium, Copper and Lead) by using carbon Nano membranes.

Keywords - Heavy Metals, Carbon Nano Membranes, ICP

1. Introduction

Now a day's numerous toxins are released into the water today, leading to a large amount of water pollution. Many heavy metals are released from various industries such as battery factories, metal processing industries, pharmaceuticals, hospitals, mining fields, etc. in water bodies leading to unsafe water for normal consumption. Therefore, Heavy metals (HM) are described as metallic elements that have a moderately high density associated to water. With the statement that heaviness and toxicity are inter-related, heavy metals also contain metalloids, such as arsenic (As), that are able to produce toxicity at low level of publicity (1).

Severe effects of heavy metals such as reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Publicity to some metals, such as mercury (Hg) and lead (Pb), may also cause improvement of autoimmunity, in which a person's protected system attacks its own cells. This can start to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system (2).

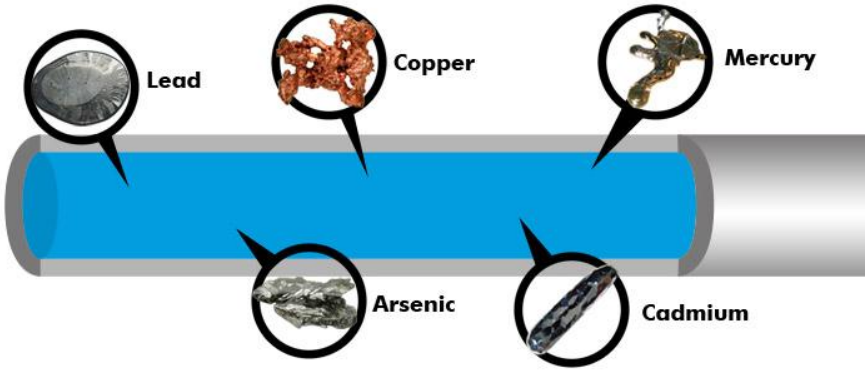

Figure 1 Heavy Metal in water

The young are more disposed to the toxic causes of heavy metals, as the quickly improving body systems in the fetus, infants and young children are far extra sensitive. Childhood publicity to various metals can effect in learning difficulties, memory impairment, damage to the nervous system, and behavioral problems such as aggressiveness and hyperactivity. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. The most common heavy metals are copper and lead, which can be very lethal to health and the surrounding environment as well. In order to get clean and safe water, these toxic chemicals must be removed (3).

The Maximum Contaminated Level (MCL) standards, for those heavy metals, established by USEPA and WHO are summarized in Table 1.

Table 1 The MCL standards for the generally hazardous heavy metals (4)

Heavy Metals	Toxicities	MCL (mg/L)
Cadmium (Cd)	Kidney damage, renal disorder, human carcinogen	0.009
Copper	Liver damage, Wilson disease, insomnia Dermatitis, nausea, chronic	0.29
Lead (Pb)	Depression, lethargy, neurological signs and nervous system	0.02

Therefore, the research aims to removal three heavy metals (Cadmium, Copper and Lead) by using carbon Nano membranes and a laboratory experiment was carried out using the Inductively coupled plasma mass spectrometry (ICP-MS) device (Agilent 7500ce) to measure the proportion of the three heavy metals pollutants.

2. Materials and Methods

2.1 Procedure of experiment

The experiments procedures of the proposed project are following:

1. Collect wastewater.
2. The sample must keep in storage tank.
3. By control valve regulator the flow of water before inserted to the filtration.
4. The second stage is bio-sand filtration to remove impurities or very fine particles
5. Compare the result with initial sample and write the observation and notes.
6. Present the procedure and analysis the result in project.

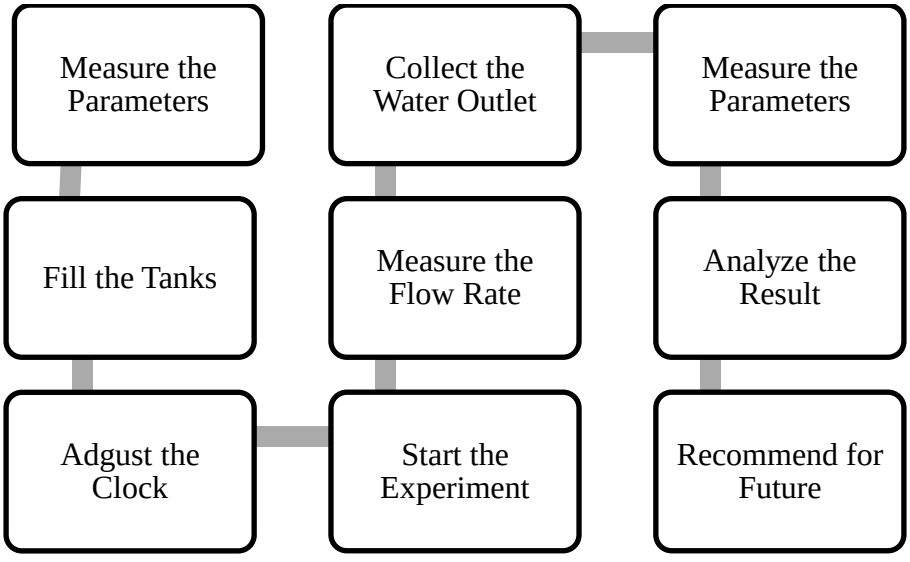

Figure 2 The main steps of the experiment

Figure 2 shows the main steps of the experiments, so, measuring the parameters is the first step following fill the tanks then set the time (clock adjust). However, after starting the experiments of the project we start measure the flow rate then collecting the water outlet, next is parameters measurements. Analyses all the results after the experiment done then recommend for future work.

2.1.1 First Stage

- The water supply from storage tank.
- Using mesh to remove the particle material in bottom and using between each layers.
- Collect bio-sand and Keep it in layer and sequence.
- 3 Different layer size of sand.
  Layer1: 4cm fine sand (quantity 3.4 kg)
  Layer2: 4cm coarse sand (quantity 4.592 kg)
  Layer3: 4cm gravel (quantity 5.332 kg)
- Contacted the pipe from filter tank.
- Open valve and take samples of wastewater in different time.
- Tasted water after treatment.

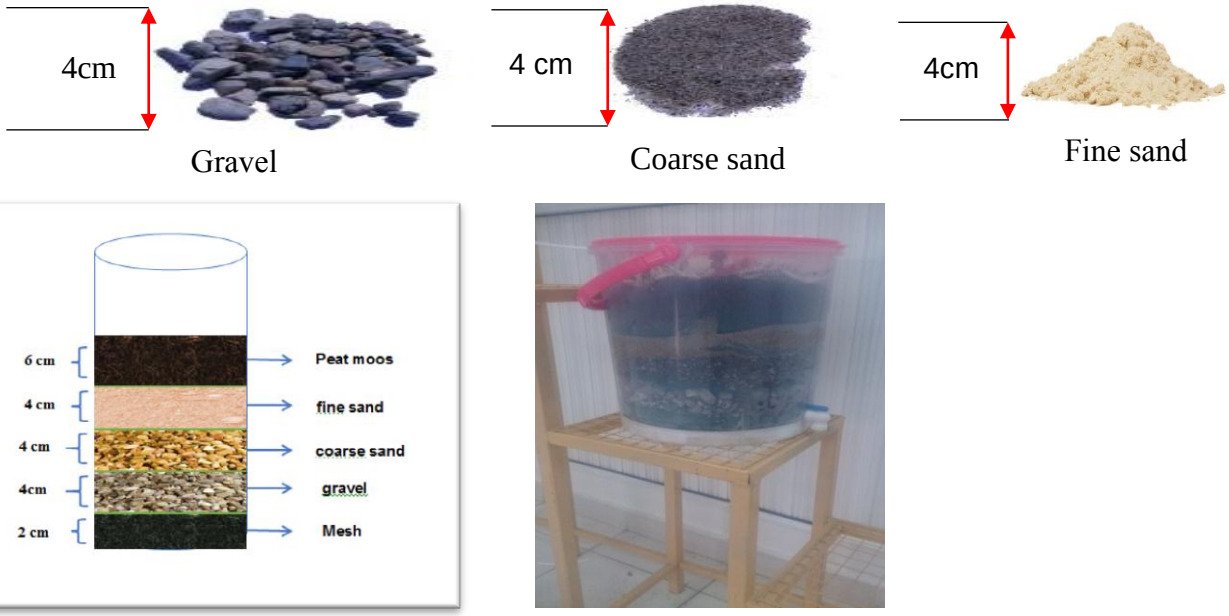

Figure 3 Bio-sand filtration

2.1.2 Second Stage: sand filter with Activated carbon and ALOH Np

- The water supply from storage tank.
- Put Activated Carbon and ALOH Np at top.
- Using mesh to remove the particle material in bottom and using between each layers.
- Collect bio-sand and keep it in layer and sequence.
- 3 Different layer size of sand.
  Layer1: 4cm fine sand (quantity 3.4 kg)
  Layer2: 4cm coarse sand (quantity 4.592 kg)
  Layer3: 4cm gravel (quantity 5.332 kg)
- Put CNM between each layer
- Contacted the pipe from filter tank.

- Open valve and take samples of wastewater in different time.
- Tasted water after treatment.

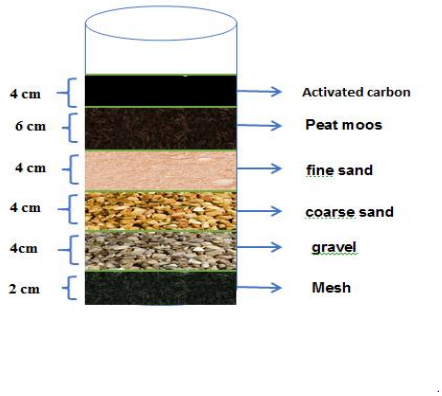

Figure 4 Bio-sand filtration with activated carbon and ALOH Np

2.2 Equipment

2.2.1 Drying oven

Drying oven is useful instrument in the lab because it can be used for drying the pill of dates at 105C for 24 hrs.

Figure 5 Drying oven

2.2.2 Digital balance

The chemicals and materials were weighed before and after experiment using the digital balance model BL-00H. Figure 5 showed the digital balance.

Figure 6 Digital balance

2.2.3 Glass equipment

Figure 6 shown some of different type of glass are used to mix and measure the sample solution and also for any other purpose during the analysis.

Figure 7 Glass equipment

2.2.4 PH Estimation

PH is a measure of the activity of the hydrogen ion (solvated). PH was measured using control dynamic pH meter (pH600).

Figure 8 pH Meter

2.2.5 Conductivity Estimation

Conductivity is a measure of the ability of water to pass an electrical current. It is measured by digital conductivity meter (MODEL 611E). The effluent was recirculate for 10, 20, and 30 minutes through the adsorption stage thus they will be three different readings for photo catalyst.

Figure 9 Conductivity Meter

2.2.6 COD Thermo –Reactor & COD meter

COD is the total measurement of all chemicals in the water that can be oxidized. COD was measured using COD meter (Thermo Electron Corporation) and analyzed in photometer. Test results are expressed as the number of milligrams of oxygen consumed per liter of sample (mg/L COD).

Figure 10 COD Thermo –Reactor & COD meter

2.2.7 TSS estimation

TSS indicates the settle able components of the total solids. The percentage of total suspended solids, which includes the colloidal fraction, is used in the design of sedimentation tanks. TSS is measured by filtering 100 ml of stirred sample through the filter paper and noting the weight of the filter paper.

Figure 11 TSS Parameter

2.2.8 TDS estimation

TDS is defined as the quantity of dissolved solids. The total dissolved solids comprises of both organic and inorganic fractions of solids in the given sample. It is necessary for the purpose of wastewater treatment plants. TDS is analyzed by measuring difference in weight of 20 ml sample after filtration and drying in an oven.

Figure 12 TDS Parameter Meter

2.2.9 Digital turbidity meter

An optical device used for measures the fluid turbidity which containing suspended particles by passing the light through the sample and measuring the loss of transmitted light intensity which is due to the scattering effect of particles suspended. Digital turbidity meter is available in engineering chemical lab of CCE which is shown in figure 12.

Figure 13 Digital turbidity meter

2.2.10 ICP - MS

The Agilent 7500ce ICP-MS device provides a graphical analysis that can reach low-per-trillion parts. The quadrupled mass spectrometer provides the ability to scan through all the elements within seconds.

Figure 14 ICP - MS

3. Results and Analysis

3.1 Data

3.1.1 Data before treatment

3.1.1.1 Water parameters

Table 2 Data Before treatment

PH	Conductivity meter	COD (mg/L)	BOD (mg/L)	TSS g/m^3	TDS Kg/ m^3	Turbidity meter (NTU)	TOC (ppm)
8.33	0.408	1119	1.73	0.077	0.109	2	143.5

Carbon Nano Membranes (CNM) parameters

Table 3 Carbon Nano Membranes (CNM) parameters

Carbon Nano Membranes Size (mesh)	50
Area covered	50 * 50 μm^2
thickness	1nm
Layers	5

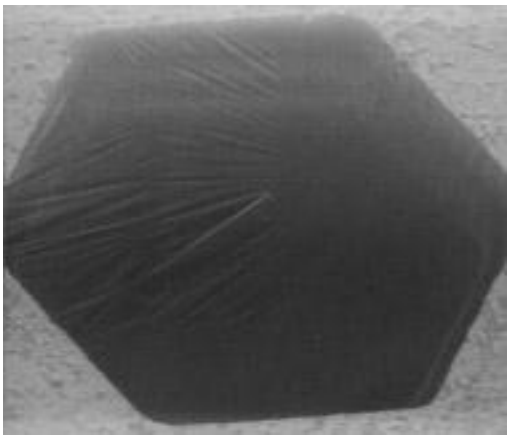

Table 4 heavy metals concentration range in the sediments on sample

	Concentration	
	mg/L	PPM
Cadmium	5.4	540
Lead	10.0	1000
Cupper	3.05	305
Heavy Metal Solution	100 ml	
Shake velocity	175 RPM	

Data after treatment with bio-sand

Table 5 data after treatment with bio-sand

Time	PH	Conductivity meter	COD (mg/L)	BOD (mg/L)	TSS g/m³	TDS Kg/ m³	Turbidity meter (NTU)	TOC (ppm)
30	8.05	0.311	1026	1.23	1.572	0.104	1.95	25.06
60	7.95	0.290	954	1.23	1.550	0.101	1.88	23.76
90	7.91	0.275	881	1.21	1.513	0.098	1.75	22.16
120	7.88	0.163	876	1.19	1.499	0.087	1.70	19.24

3.1.2 Data after treatment Bio sand system with activated carbon and ALOH Np

Table 6 Data after treatment Bio sand system with activated carbon and ALOH Np

Time	PH	Conductivity meter	COD (mg/L)	BOD (mg/L)	TSS g/m³	TDS Kg/ m³	Turbidity meter (NTU)	TOC (ppm)
30	7.61	0.154	798	0.22	0.932	0.084	1.69	22.17
60	7.57	0.150	785	0.20	0.927	0.082	1.66	18.16
90	7.48	0.133	769	0. 17	0.924	0.079	1.57	17.36
120	7.40	0.124	766	0.14	0.920	0.076	1.51	12.85

3.1.3 Data after treatment with CNM

Table 7 CNM data after treatment

Time	6 Hrs.	12 Hrs.	18 Hrs.	24 Hrs.
Cadmium (Cd)	4.15	2.73	1.90	0.01
Lead (Pb)	8.12	4.13	1.53	0.01
Cupper (Cu)	2.95	2.28	1.39	0.25

Figure 15 Before Treatment

Figure 16 After Stage 1 (Bio Sand)

Figure 17 After Stage 2 (AC + ALOH Np)

3.2 Analysis

3.2.1 Effect of pH Procedure

1. First process, the preliminary Samples(50ml) taken from supply at 30 minutes .So, the parameter of pH set reading 8.05 mg/l
2. Second Step, taken (50ml) from the supply at 60 minutes and the parameter of pH given reading 7.95 mg/l.
3. Record test (50ml) at 90 minutes and the parameter of pH gives a very excellent reading 7.91 mg/l.
4. Last test (50ml) at 120 minutes and the parameter pH give 7.88 mg/l.

Table 8 pH Parameter

Actual Sample	Time	Bio sand system	Bio sand system with activated carbon and ALOH Np
8.33	30	8.1	7.68
	60	7.98	7.56
	90	7.93	7.50
	120	7.86	7.74

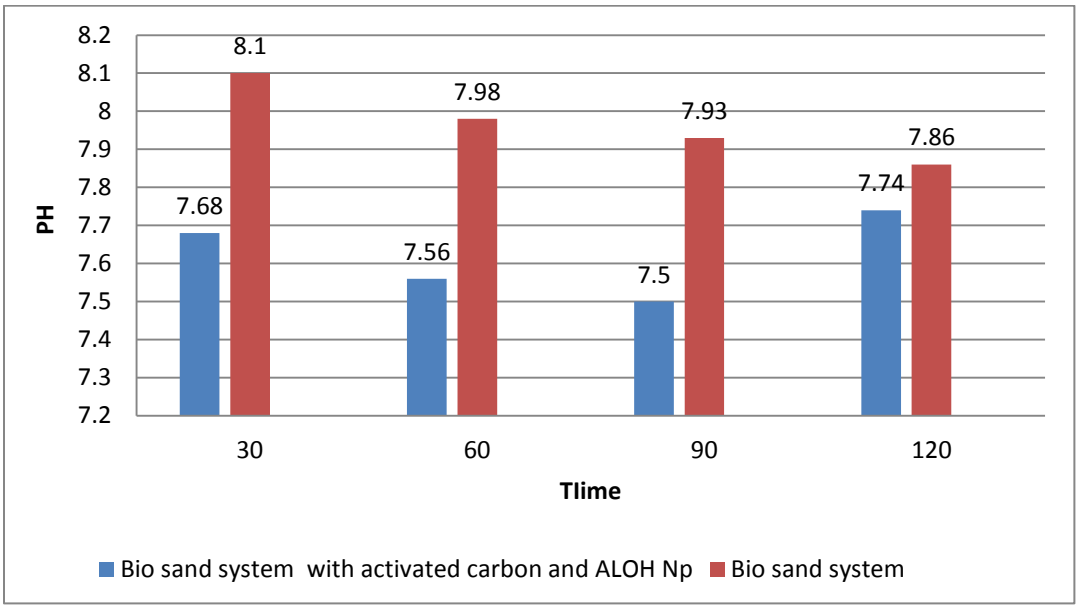

Figure 18 Effect of pH Parameter

It is clear from table 4 & figure 16 that the change of pH of the sample by the two methods. Actual sample have 8.33 ph. Bio sand with activated carbon and ALOH Np designs were the greatest in decreasing ph. However, at the minuets of 30, 60 , 90 and 120 the bio sand system with activated carbon and ALOH Np reach 7.68, 7.56, 7.50and 7.74 respectively. While the Bio sand system was the less than Bio sand with activated carbon and ALOH Np in reducing ph. At the minute 30 is equal 8.1, and at 60 is equal 7.9, 90 equal 7.91 and at 120 minutes the bio sand system reached 7.86.

3.2.2 Effect of Conductivity meter Procedure

1. First tested initial Samples (50ml) taken from supply at 30 minutes .The parameter of the conductivity given reading of 0.311 and 0.154
2. then, at 60 minutes (50ml) is taken, the parameter of the conductivity given a reading 0.290 and 0.150
3. Next at 90 minutes (50ml), the parameter of the conductivity provided good reading 0.275 and 0.133
4. Last, at 120 minutes (50ml)is taken and the parameter the conductivity present 0.163 and 0.124.

Table 9 After Treatment (Conductivity meter Parameter)

Actual Sample	Time	Bio sand system	Bio sand system with activated carbon and ALOH Np
0.408	30	0.310	0.155
	60	0.290	0.150
	90	0.280	0.135
	120	0.160	0.122

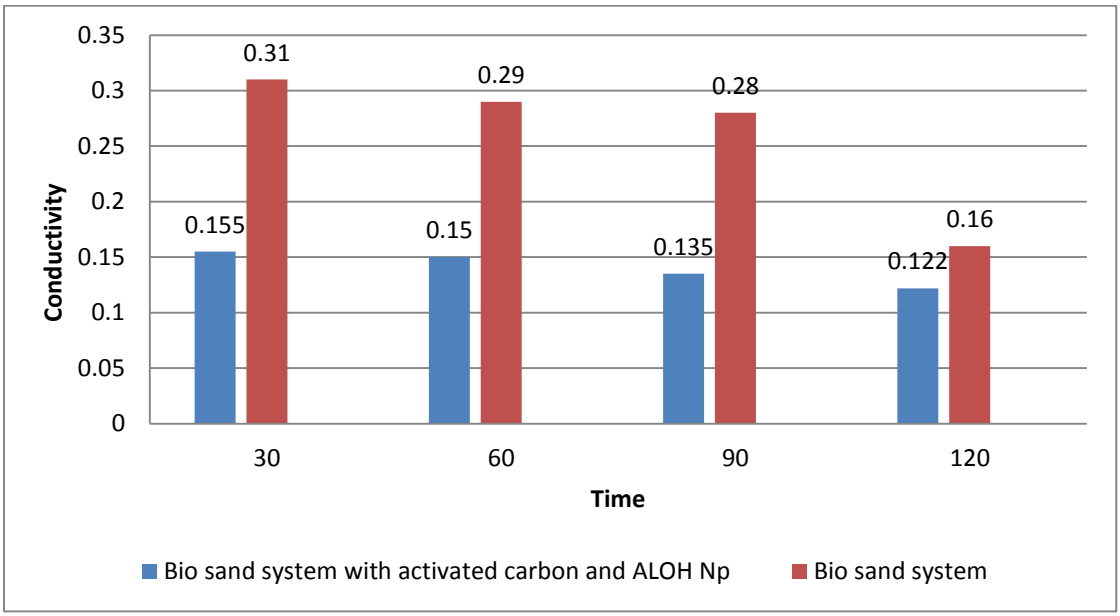

Figure 19 Effect of Conductivity meter

Table 5 & figure 17 illustrate the change of Conductivity meter of the sample by the two techniques. Actual sample have 0.408 conductivity meter. Bio sand with activated carbon and ALOH Np design was the best in reducing ph. It shown a value of 0.155 at the first half hour, while for first hour the value of the reading is 0.150. For the second hour at 90 minutes it shown 0.135 and at 120 minutes equal 0.122. For the Bio sand system was the less than Bio sand with activated carbon and ALOH Np in reducing Conductivity meter. It reached only 0.310 at 30 minutes and at 60 minutes it reached 0.290, at 90 it reached 0.280 and 0.160 at 120 minutes.

3.2.3 Effect of COD Procedure

1. First process a 2 ml of sample and 2 ml of distilled water were put in different time at 30, 60, 90 and 120 minutes.
2. The distilled and sample putted on the potassium dichromate solution.
3. Then, add 2 hour on thermo actor.
4. Last, measure the cod and note down the reading.

Table 10 After Treatment (Effect of COD % Removal)

Actual Sample	Time	Bio sand system	Bio sand system with activated carbon and ALOH Np
1119	30	8.30	28.65
	60	14.75	29.85
	90	21.25	31.25
	120	21.70	31.55

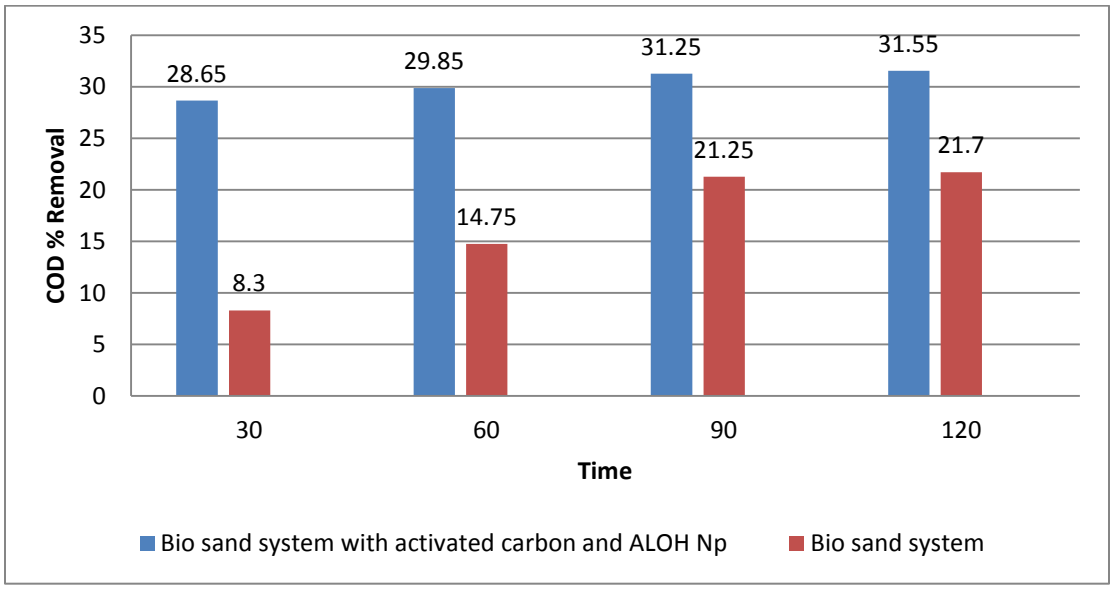

Figure 20 Effect of COD % Removal

Table 6 & figure 18 show the change of COD % Removal the sample by the two methods. Actual sample have 1119 COD. Bio sand with activated carbon and ALOH Np design were the best in reducing the removal% of COD. It reached (30= 28.65), (60=29.85) , (90=31.25) and (120=31.55) .Bio sand system was the less than Bio sand with activated carbon and ALOH Np in reducing The removal% of COD. It reached (30=8.30), (60=14.75), (90=21.25) and (120=21.70).

3.2.4 Effect of BOD Procedure

1. A 50 ml of a sample taken in different time 30, 60, 90 and 120 minutes and measure the BOD of the sample (wastewater).
2. The sample should be kept on the fridge for 5 day.
3. Then after 5 day we measure the BOD again.
4. Make a note of down the reading.

Table 11 After Treatment (Effect of BOD % Removal)

Actual Sample	Time	Bio sand system	Bio sand system with activated carbon and ALOH Np
1.73	30	28.95	87.5
	60	28.96	88.7
	90	30.1	90.2
	120	31.2	92

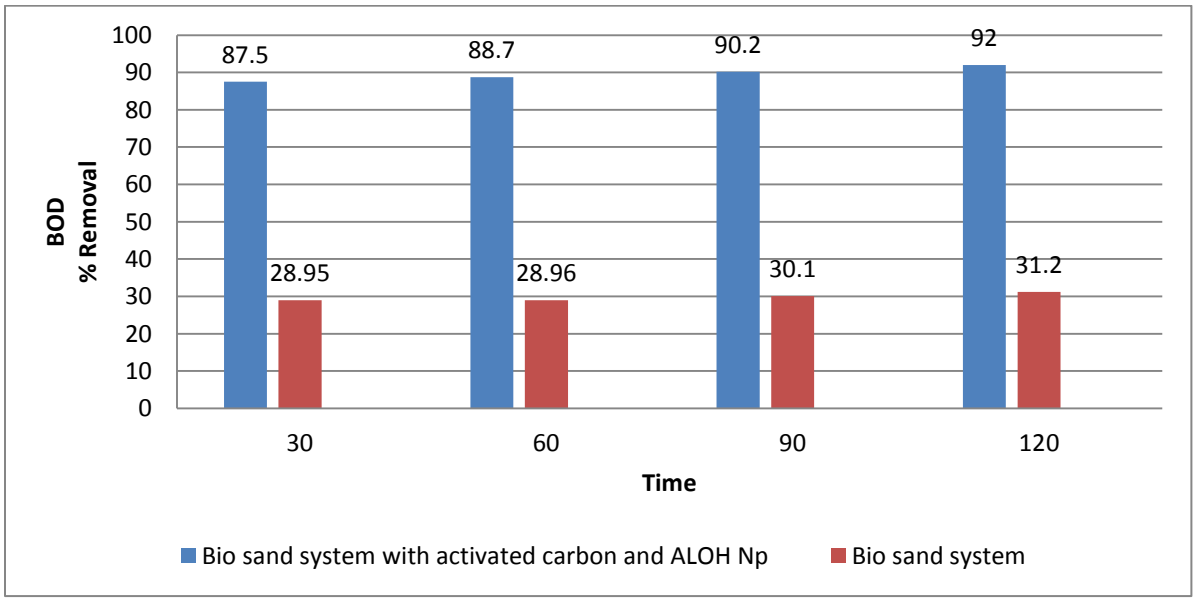

Figure 21 Effect of BOD % Removal

Table 7 & figure 19 respectively indicate the change of BOD of the sample by the two processes. Actual sample have 1.73 BOD. The Bio sand with activated carbon and ALOH Np design were the best in reducing the removal% of BOD. It reached 87.5 at the first 30 minutes and 88.7 for first hour, at 90 minutes it reached 90.2 and 92 at two hours .Bio sand system was the less than Bio sand with activated carbon and ALOH Np in reducing The removal% of BOD. It reached (30=28.95), (60=28.96), (90=30.1) and (120=31.2).

3.2.5 Effect of TSS Procedure

1. A four fitter paper is taken and weighted.
2. Then a 50ml of the sample taken in different time (30, 60, 90 and 120).
3. Bring 4 vessel and 4 conceal flask to start doing filtering after filtering keep the filter paper in the orbital shaker around one day.
4. Weight the filter paper after drying and note down the reading.

Table 12 After Treatment (Effect of BOD % Removal)

Actual Sample	Time	Bio sand system	Bio sand system with activated carbon and ALOH Np
0.077	30	1.570	0.935
	60	1.552	0.930
	90	1.515	0.921
	120	1.500	0.917

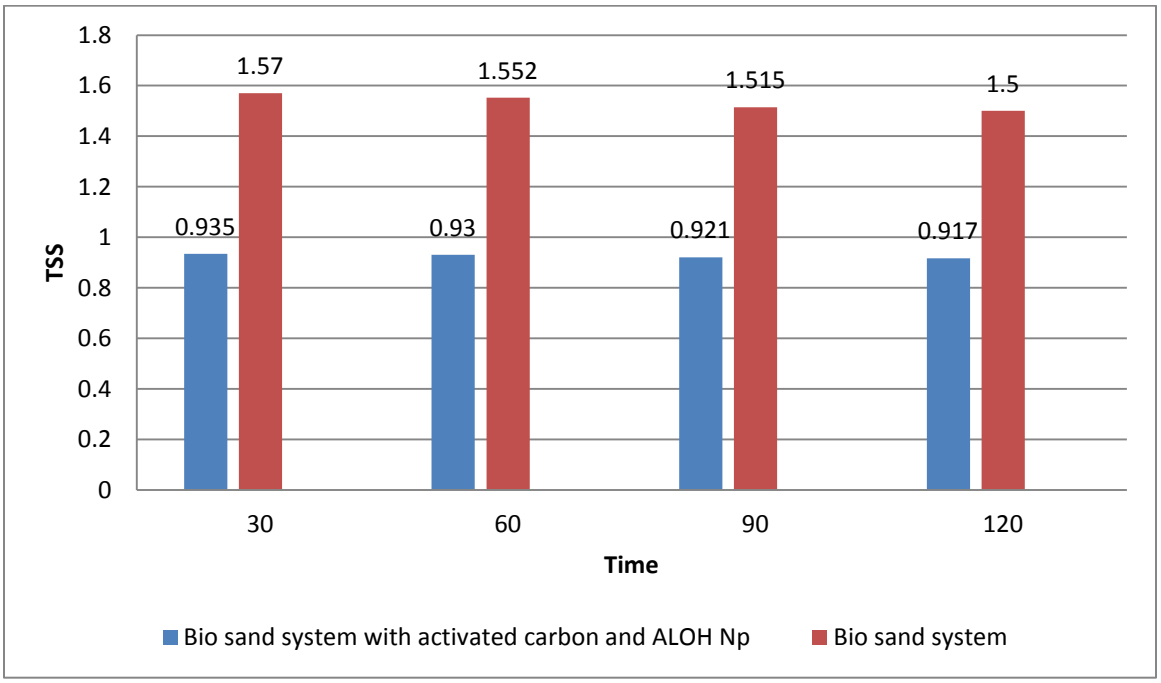

Figure 22 Effect of TSS % Removal

Table 8 & figure 20 show the change of TSS of the sample by the two methods. Actual sample have 0.077 TSS. Bio sand with activated carbon and ALOH Np design were the best in reducing TSS. It reached (30= 0.935), (60=0.93) , (90=0.921) and (120=0.917). Bio sand system was the less than Bio sand with activated carbon and ALOH Np in reducing The removal% of BOD. It reached (30=1.570), (60=1.552), (90=1.515) and (120=1.500).

3.2.6 Effect of TDS

Total dissolved solids(TDS) is the gross amount of the ions loaded phones, including minerals salts or minerals dissolved in a given volume of water, expressed in units mg per unit volume of water (mg / L), also referred to parts per million (ppm). TDS directly related to the purity of the water quality of and water filtration systems and affects everything is consumed, lives in or uses the water, whether organic or inorganic chemistry, whether for better or worse.

Procedure

1. Take 4 crucibles to dry the sample.
2. Weight the crucible before put the sample.
3. Put 50ml of sample for each 4 crucible in different time (30, 60, 90 and 120).
4. Keep 4 the sample for one day on the orbital shaker .
5. Than weight the crucible after drying and record the reading.

Table 13 After Treatment (Effect of TDS % Removal)

Actual Sample	Time	Bio sand system	Bio sand system with activated carbon and ALOH Np
0.109	30	0.103	0.082
	60	0.100	0.080
	90	0.096	0.077
	120	0.085	0.075

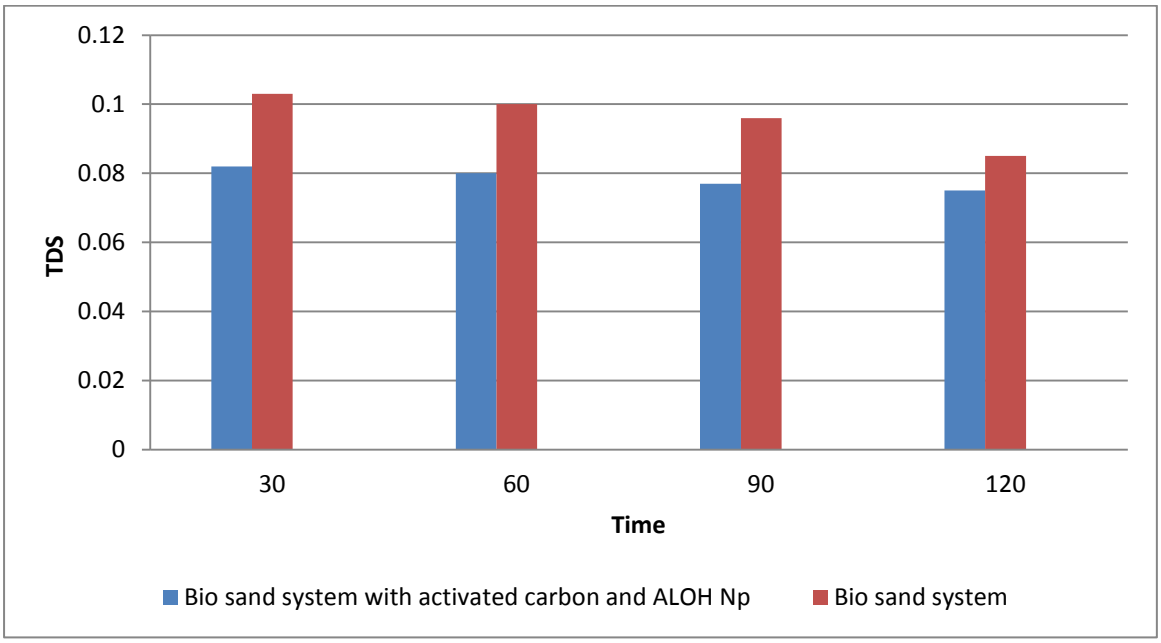

Figure 23 Effect of TDS % Removal

Table 9 & figure 21 shows the change of TDS of the sample by the two methods. Actual sample have 0. 0.109. Bio sand with activated carbon and ALOH Np design were the best in reducing TDS. It reached (30= 0.082), (60=0.080) , (90=0.077) and (120=0.075) .Bio sand system was the less than Bio sand with activated carbon and ALOH Np in reducing The removal% of BOD. It reached (30=0.103), (60=0.10), (90=0.096) and (120=0.085).

3.2.7 Effect of turbidity (NTU)

Turbidity is the quantity of clouds in the water. This can vary by clay and silts it would be impossible to see may be through sewage (the high turbidity), the spring water that appears to be absolutely clear (a low turbidity).

Procedure

1. At initial samples a 50 ml taken from supply at 30 minutes .The parameter of pH recorded reading 1.95 NTU
2. After that, 50ml taken at 60 minutes .Besides the parameter of pH given a reading 1.88 NTU
3. Then, at 90 minutes 50ml tested and the parameter of pH provided a good reading 1.75 NTU
4. Last a50ml taken at 120 minutes and the parameter pH give 1.70 NTU

Table 14 After Treatment (Effect of turbidity (NTU))

Actual Sample	Time	Bio sand system	Bio sand system with activated carbon and ALOH Np
2.00	30	1.93	1.65
	60	1.86	1.62
	90	1.72	1.53
	120	1.70	1.49

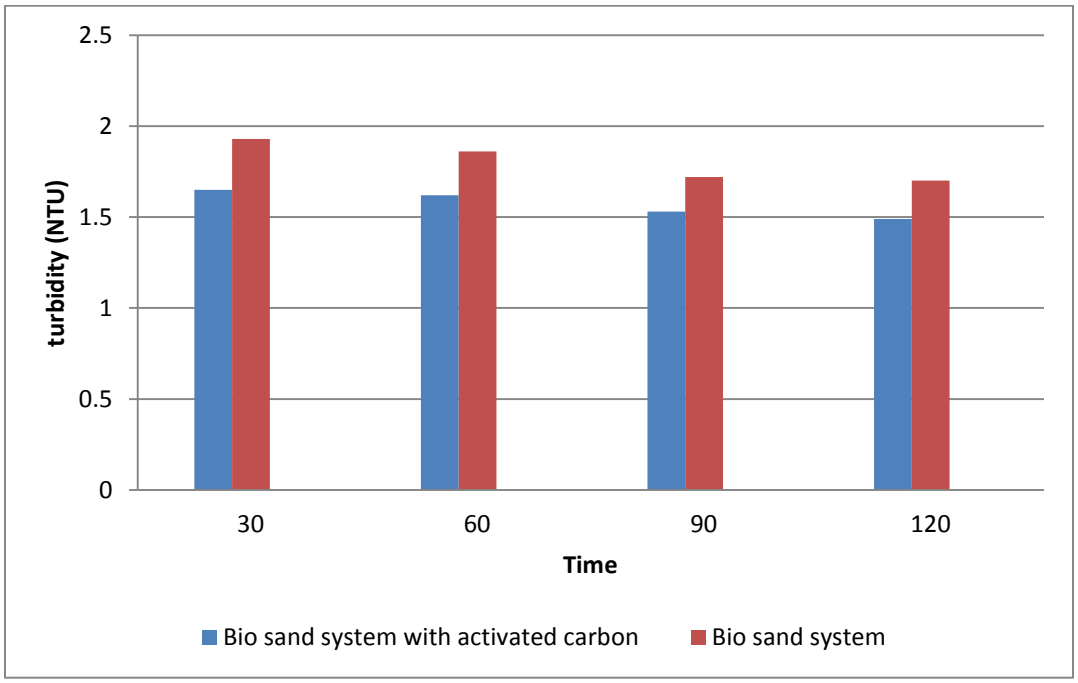

Figure 24 Effect of turbidity (NTU)

Table 10 and Figure 22 show the modify in turbidity of the samples by the three procedures. The actual samples have 2.00 NTU. It's very obvious that the result of bio sand with activated carbon and ALOH Np design were the greatest in reducing NTU. It reached time against turbidity by varying the values from (30= 1.65), (60=1.62), (90=1.53) to (120=1.53).Moreover, by bio sand without activated carbon and ALOH Np shown lass in reducing NTU. It reached the values of 1.93at the first 30 minutes and at 60 minutes is 1.86, so, at 90 and 120 minutes it reached 1.72 and 1.70 respectively

3.2.8 Effect of TOC Procedure

1. First step 5 samples taken in different time (30, 60, 90 and 120) and measure the TOC of the sample.
2. The samples must be kept in TOC device.
3. Then switch on the device and started to measure the TOC.
4. Note down the values.

Table 15 After Treatment (Effect of TOC % Removal)

Actual Sample	Time	Bio sand system	Bio sand system with activated carbon and ALOH Np
143.50	30	25.06	22.17
	60	23.76	18.16
	90	22.16	17.36
	120	19.24	12.85

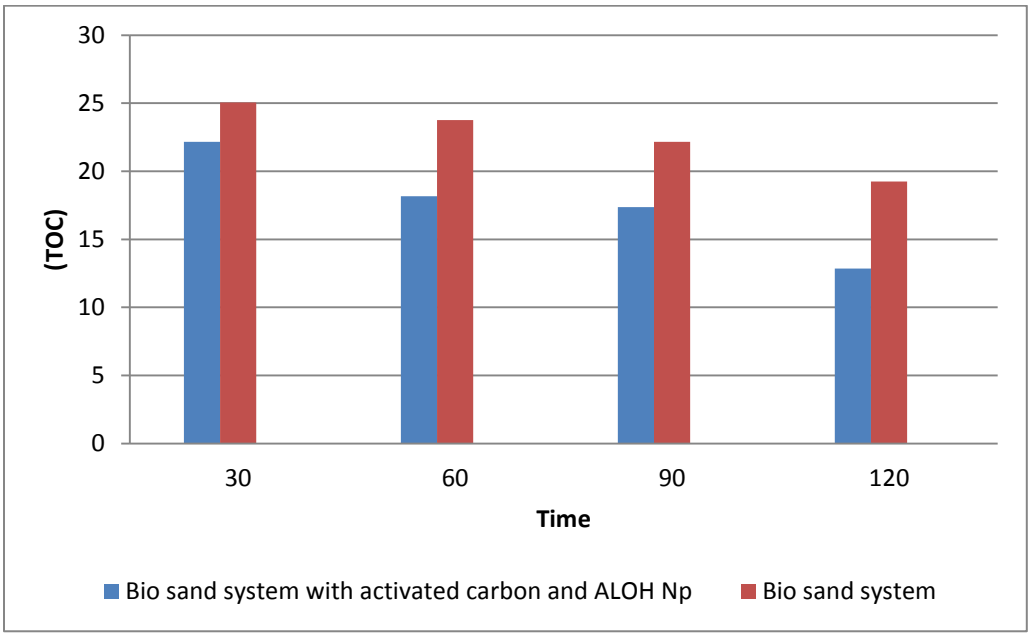

Figure 25 Effect of TOC % Removal

3.2.9 Effect of CNM

Table 7 CNM data after treatment, Figure 26 Cd result, Figure 27 Pb result, Figure 28 Cu result are show the modify in heavy metals concert of the samples. The actual samples have 540 ppm of cadmium, 1000 ppm of lead and 305 ppm of cupper. It's very obvious that the result of CNM were the greatest in reducing heavy metals. It reached low toxics by varying the values of Cd from (6 Hrs.= 415 ppm), (12 Hrs. = 273 ppm), (18 Hrs. = 190 ppm) to (24 Hrs. = 1 ppm), Pb from (6 Hrs.= 812 ppm), (12 Hrs. = 413 ppm), (18 Hrs. = 153 ppm) to (24 Hrs. = 1 ppm) and Cu from (6 Hrs.= 295 ppm), (12 Hrs. = 228 ppm), (18 Hrs. = 139 ppm) to (24 Hrs. = 25 ppm).

All the results of the experiment for Cadmium, lead and Copper have been summarized in table 7, and it's shown that all concentration of heavy metals are meet the WHO standard water as shown in table1 after treatment with CNM as used in slice between each layers.

3.2.9.1 Cadmium

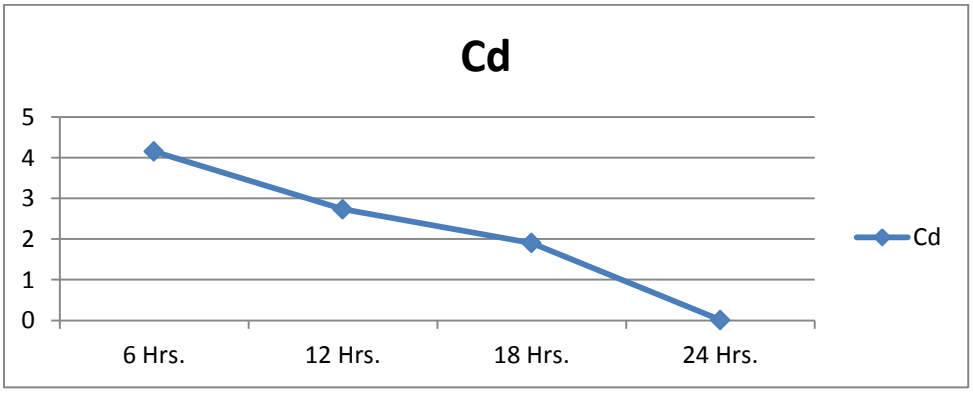

Figure 26 Cd result

3.2.9.2 Lead

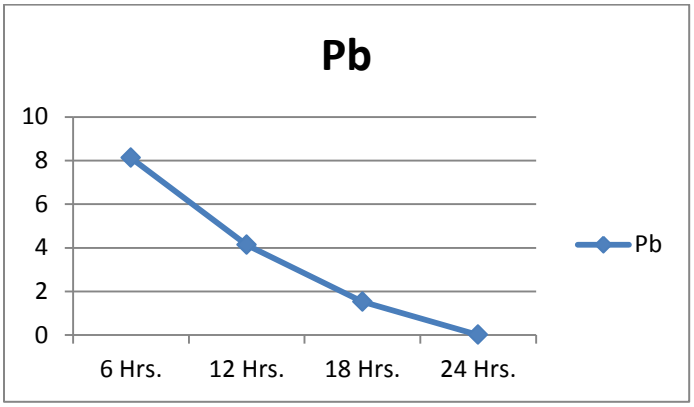

Figure 27 Pb result

3.2.9.3 Cupper

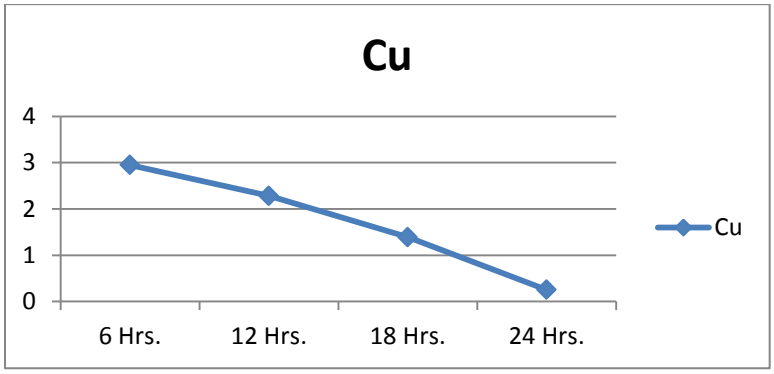

Figure 28 Cu result

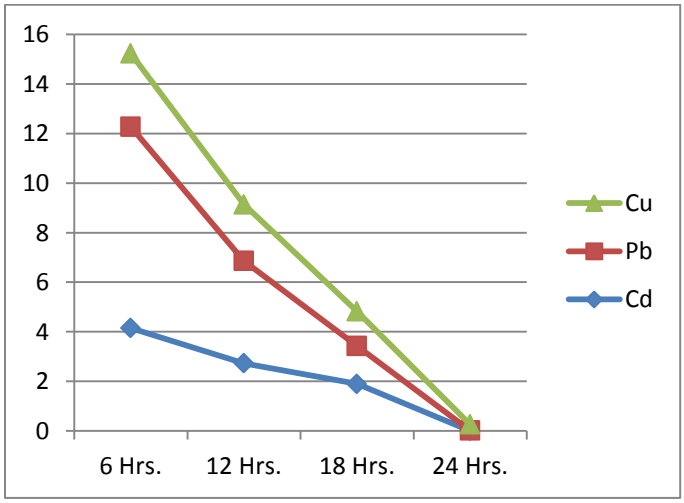

Figure 29 Heavy Metals results

4. Conclusion

CNM is an efficient for the removal of heavy metals (especially for Cadmium, Lead and Cooper) from wastewater (5). The process of removal heavy metals from wastewaters occurs in two stages by designing two simple columns containing bio sand as column 1 and bio sand with activated carbon and ALOH Np for disposal of chemicals parameters (TSS, turbidity, COD, BOD, pH, TDS, conductivity) and CNM for removal heavy metals (Cd, Pb, Cu) as column 2 has been explored and experimented. The results clearly showed that sand filter with activated carbon, ALOH Np with CNM are the most effective method used in this research. On the other hand CNM have good removal efficiency of heavy metals (6).

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