# Treatment of pharmaceutical industry's waste water using low cost adsorbents.

Tandel Vatsalkumar Dipakbhai[1]

[1]*Masters of chemical engineering, Vishwakarma Government Engineering College, Chandkheda, Ahmedabad, Gujarat, India-382424.*

**ABSTRACT**

*The pharmaceutical companies plays a leading role in the sustainment of human life. A large amount of waste effluents have been generated having diclofenac, salicylic acid, ibuprofen and acetaminophen contaminants. Because of increasing environment awareness, it is necessary to remove the pollutants from waste water stream. Adsorption is one such method, but the problem faced is regeneration / recovery of adsorbent. An alternative to this is to make use of low cost adsorbent. This work here focuses on low cost adsorbent aiming to decrease pollutants being discharged into water bodies. The researchers have found various cheap adsorbents for the treatment of the effluents changing the parameters like pH, adsorbent dosage, temperature, pressure, etc. There are very few research carried out on the pharmaceutical industry, so we have been focusing on treatment of the waste water collected from the pharmaceutical industry which manufactures intermediate chemicals.*

**Keyword: -** *Low cost Adsorbent, Adsorption, Waste water treatment, Batch process.*

## 1. Activation of the adsorbent:-

$ZnCl_2$ is forbidden because of its polluting character. KOH may work but will be probably too aggressive. $H_3PO_4$ is recommended, having the advantage of not requiring inert atmosphere, and working at moderate temperature of 550°C. Just impregnate thoroughly the material with 85% $H_3PO_4$ and heat it at 550°C in a muffle furnace in air. Then, wash it thoroughly with hot water in a Soxhlet. We can change the value of the parameters (time, impregnation ratio, temperature) to find the optimum conditions.[7]

Adsorbents prepared from orange peel, which is a domestic waste, successfully used to remove the methylene blue from an aqueous solution in a batch wise column.[7] The ability of activated carbon produced from orange peel to adsorb heavy metals like Pb(II), Fe(II), Cu(II), and Zn(II) ions from electroplating industrial wastewater can be studied through batch experiment.[2]

Natural materials and waste agricultural products as an alternative to replace commercial activated carbon.[3] The abundance and availability of agricultural byproducts make them good sources of raw materials for natural sorbent orange peel is treated with $ZnCl_2$ solution to produce a carbonaceous adsorbent, which is subsequently use to treat effluent obtained from electroplating industries.[5]

The capacity of the produced adsorbent to adsorbed heavy metals like Pb(II), Fe(II), Cu(II), and Zn(II) from the effluent with emphasis on the effects of contact time, adsorbent dosage, pH and stirring rate can be carried out.[1] [6] [8]

Biomass is typically chemically activated with $ZnCl_2$, $H_3PO_4$, or KOH, then usually heat treated. Each of these methods will develop a material with some different properties.

Activation of neem leaf with steam is cheaper (as water is indeed much cheaper than pure $CO_2$), and requires lower temperatures (typically 700 - 800°C) than $CO_2$ (typically 900°C). For general-purpose activated carbons, the development of the porosity is far enough with steam, and therefore doesn't require the need of the much more expensive $CO_2$, which produces narrower pores in general.[4]

## 2. Effluent collection and primary analysis:-

Effluent has been collected from the pharmaceutical industry situated at south Gujarat which manufactures 4-4 Di-chloro Diphenyl Sulphone.

The product is used as an intermediate for the manufacturing of Aerospace parts as anti-corrosive powder. This product has no harmful effect on living organisms. MCB and PCBSA is used to manufacture the product and that are present in the effluent also.

From the primary analysis of the waste water, it is concluded that there is few major impurities that has to be reduced. Ammonical nitrogen (A.N.), COD, BOD, TDS, Mono-chloro benzene (MCB) and P-chloro benzene sulphonic acid (PCBSA). Total $75m^3$ effluent is generated per day.

These two main impurities MCB and PCBSA can be removed totally from the effluent because both are harmful for living organism. Both MCB and PCBSA can create eye/skin/respiratory tract irritation.

## 3. Experimental Setup, Procedure & Primary Analysis:-

Adsorbents taken for the treatment of the pharmaceutical industry's effluent is as below:

1. Activated Carbon (Conventional)
2. Bentonite Clay
3. Fly Ash

Activated carbon is conventional and widely used for the water treatment but it is taken for the comparison of results with the bentonite clay and fly ash.

### 3.1 Experimental Setup:-

**Fig -1**: Experimental Setup

**Fig -2**: Sample filtered after the treatment

### 3.2 Primary analysis of the sample with 1% activated carbon:-

| For 1% activated carbon | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | 2 | 5 | 21 |
| COD(ppm) | 3250 | 2630 | 1850 | 1160 | 1080 | 1050 | 990 |
| pH | 5.33 | 5.33 | 5.33 | 5.33 | 5.33 | 5.33 | 5.33 |
| TDS(ppm) | 670 | 545 | 395 | 270 | 255 | 240 | 210 |
| BOD(ppm) | 1450 | 1260 | 810 | 580 | 530 | 510 | 485 |
| MCB traces | 0.300% | 0.290% | 0.260% | 0.240% | 0.235% | 0.233% | 0.230% |
| PCBSA traces | 3.000% | 2.900% | 2.750% | 2.550% | 2.500% | 2.485% | 2.450% |
| A.N.(ppm) | 4000 | 3240 | 2400 | 1950 | 1880 | 1810 | 1740 |

**Table -1: Treatment with 1% Activated Carbon**

From this primary analysis of the waste water for about 21 hours of stirring, the conclusion is the reduction rate decreases from 20-25% to 5-8% after 1 hour 30 minutes. So the experiments were carried out for the time period of 30 minutes/1 hour/1.5 hour of stirring.

### 3.3 Experimental Procedure:-

At first, 100 ml of untreated waste water is taken in beaker collected from the pharmaceutical industry. And then filter it primarily with the use of filter paper. Then the desired amount of the adsorbent is added in to the beaker. Here the desired amount of the adsorbent is 1/2/3 gm per 100 ml of the waste water sample.

Then the beaker is being put on the stirrer which is having rotational speed of 150 rpm. There is no heating provided for this batch operation. The mixture has been kept for the stirring purpose for about 1.5 hours. The sample has been collected in between the desired time period.

First treated sample has been collected after 30 min of stirring. Second treated sample is collected after 1 hour of stirring and the third treated sample is collected after 1.5 hour of stirring at the constant speed of 150 rpm. The sample which is being collected after the desired period of time is approximately 15 ml.

Then the treated sample is taken for the analysis part where the amount of the impurities are being calculated.

## 4. Results:-

The following chart shows the comparison between the three adsorbents which has been added in the same amount in 100 ml of waste water:

| For 1% Adsorbent dose: Activated Carbon | | | | | |
|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | % removal |
| COD(ppm) | 2900 | 1320 | 1080 | 520 | 82.07% |
| pH | 5.33 | 5.33 | 5.33 | 5.33 | - |
| TDS(ppm) | 670 | 510 | 385 | 190 | 71.64% |
| BOD(ppm) | 1600 | 1100 | 680 | 240 | 85% |
| MCB traces | 0.30% | 0.28% | 0.23% | 0.20% | 33.33% |
| PCBSA traces | 3% | 2.85% | 2.35% | 2% | 33.33% |
| A.N.(ppm) | 4350 | 3492 | 1985 | 1230 | 71.72% |

| For 2% Adsorbent dose: Activated Carbon | | | | | |
|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | % removal |
| COD(ppm) | 2900 | 1130 | 920 | 410 | 85.86% |
| pH | 5.33 | 5.33 | 5.33 | 5.33 | - |
| TDS(ppm) | 670 | 455 | 345 | 175 | 73.88% |
| BOD(ppm) | 1600 | 990 | 620 | 180 | 88.75% |
| MCB traces | 0.300% | 0.270% | 0.215% | 0.190% | 36.67% |
| PCBSA traces | 3.000% | 2.700% | 2.100% | 1.850% | 38.33% |
| A.N.(ppm) | 4350 | 3120 | 1765 | 1080 | 75.17% |

| For 3% Adsorbent dose: Activated Carbon | | | | | |
|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | % removal |
| COD(ppm) | 2900 | 1010 | 870 | 330 | 88.62% |
| pH | 5.33 | 5.33 | 5.33 | 5.33 | - |
| TDS(ppm) | 670 | 410 | 290 | 145 | 78.35% |
| BOD(ppm) | 1600 | 900 | 550 | 160 | 90% |
| MCB traces | 0.300% | 0.262% | 0.200% | 0.175% | 41.67% |
| PCBSA traces | 3.000% | 2.650% | 2.000% | 1.700% | 43.33% |
| A.N.(ppm) | 4350 | 3000 | 1650 | 910 | 79.08% |

| For 1% Adsorbent dose: Fly Ash | | | | | |
|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | % removal |
| COD(ppm) | 3250 | 2630 | 1850 | 1160 | 64.31% |
| TDS(ppm) | 670 | 545 | 395 | 270 | 59.70% |
| BOD(ppm) | 1450 | 1260 | 810 | 580 | 60% |
| MCB traces | 0.30% | 0.29% | 0.26% | 0.24% | 20% |
| PCBSA traces | 3% | 2.90% | 2.75% | 2.55% | 15% |
| A.N.(ppm) | 4000 | 3240 | 2400 | 1950 | 51.25% |

| For 2% Adsorbent dose: Fly Ash | | | | | |
|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | % removal |
| COD(ppm) | 3250 | 2400 | 1720 | 1040 | 68% |
| TDS(ppm) | 670 | 510 | 360 | 240 | 64.18% |
| BOD(ppm) | 1450 | 1140 | 710 | 470 | 67.59% |
| MCB traces | 0.300% | 0.280% | 0.245% | 0.220% | 26.67% |
| PCBSA traces | 3.000% | 2.850% | 2.650% | 2.400% | 20% |
| A.N.(ppm) | 4000 | 3020 | 2130 | 1790 | 55.25% |

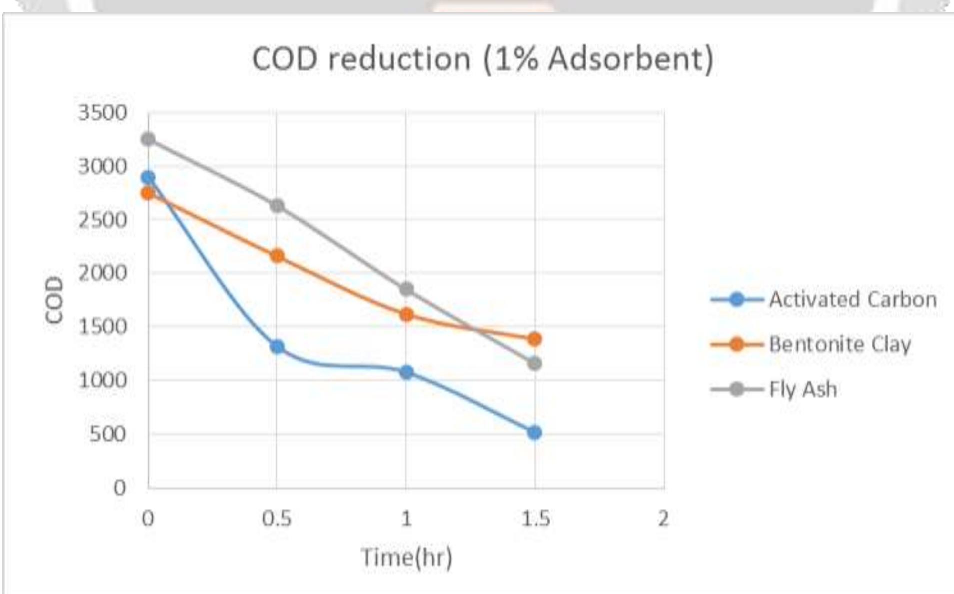
| For 3% Adsorbent dose: Fly Ash | | | | | |
|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | % removal |
| COD(ppm) | 3250 | 2240 | 1550 | 1000 | 69.23% |
| TDS(ppm) | 670 | 495 | 340 | 230 | 65.67% |
| BOD(ppm) | 1450 | 1080 | 680 | 455 | 68.62% |
| MCB traces | 0.300% | 0.275% | 0.238% | 0.210% | 30% |
| PCBSA traces | 3.000% | 2.800% | 2.650% | 2.200% | 26.67% |
| A.N.(ppm) | 4000 | 2930 | 2090 | 1720 | 57% |

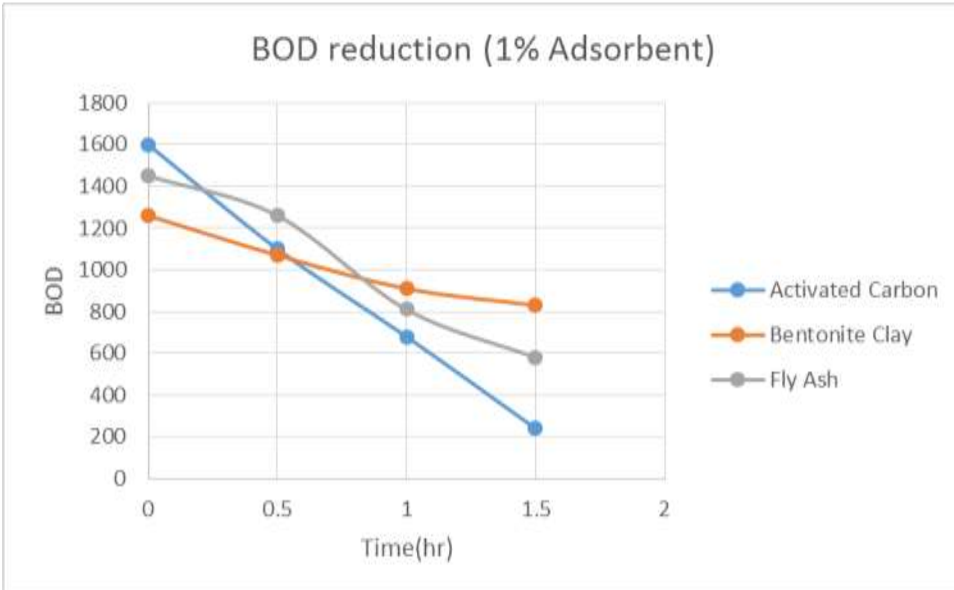
| For 1% Adsorbent dose: Bentonite Clay | | | | | |
|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | % removal |
| COD(ppm) | 2750 | 2160 | 1620 | 1385 | 49.64% |
| pH | 5.33 | 5.33 | 5.33 | 5.33 | - |
| TDS(ppm) | 730 | 680 | 560 | 410 | 43.84% |
| BOD(ppm) | 1260 | 1070 | 910 | 830 | 34.13% |
| MCB traces | 0.280% | 0.275% | 0.262% | 0.255% | 8.93% |
| PCBSA traces | 2.800% | 2.750% | 2.650% | 2.600% | 7.14% |
| A.N.(ppm) | 4220 | 3930 | 3150 | 2560 | 39.33% |

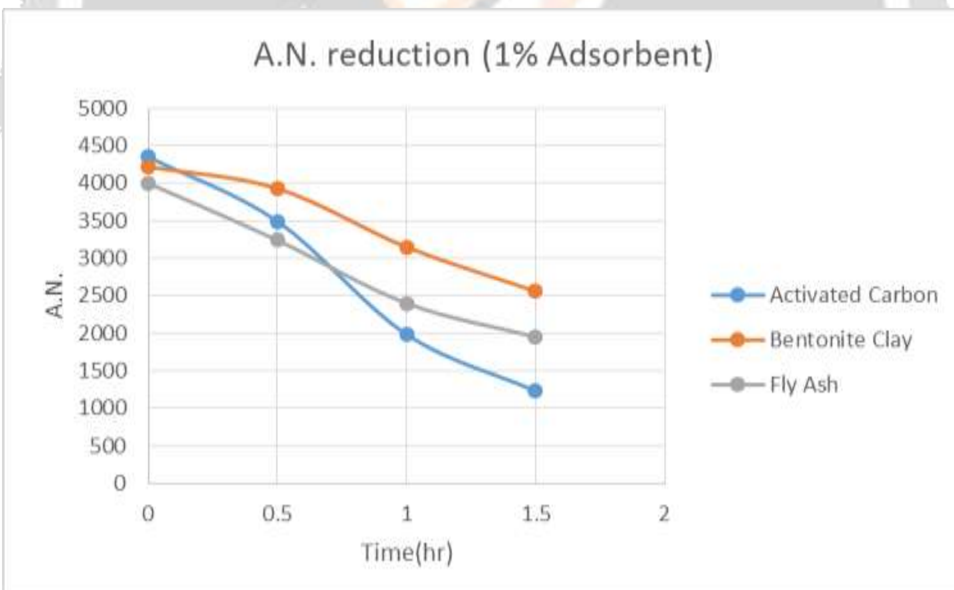
| For 2% Adsorbent dose: Bentonite Clay | | | | | |
|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | % removal |
| COD(ppm) | 2750 | 2020 | 1450 | 1120 | 59.27% |
| pH | 5.33 | 5.33 | 5.33 | 5.33 | - |
| TDS(ppm) | 730 | 650 | 500 | 340 | 53.42% |
| BOD(ppm) | 1260 | 960 | 820 | 710 | 43.65% |
| MCB traces | 0.280% | 0.269% | 0.257% | 0.244% | 12.86% |
| PCBSA traces | 2.800% | 2.710% | 2.590% | 2.505% | 10.53% |
| A.N.(ppm) | 4220 | 3860 | 2960 | 2350 | 44.31% |

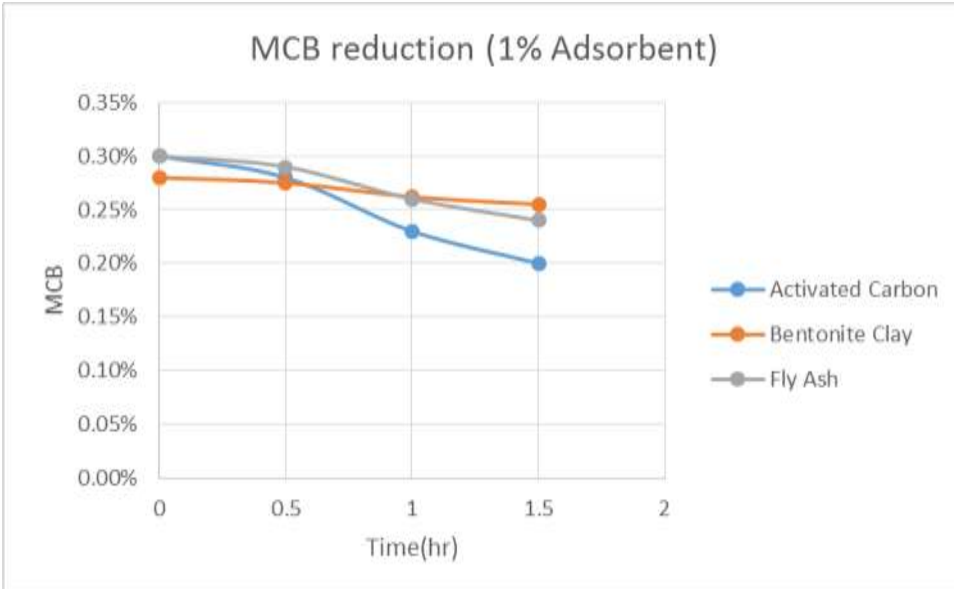
| For 3% Adsorbent dose: Bentonite Clay | | | | | |
|---|---|---|---|---|---|
| Time(hour) | 0 | 0.5 | 1 | 1.5 | % removal |
| COD(ppm) | 2750 | 1920 | 1370 | 1050 | 61.82% |
| pH | 5.33 | 5.33 | 5.33 | 5.33 | - |
| TDS(ppm) | 730 | 620 | 470 | 310 | 57.53% |
| BOD(ppm) | 1260 | 930 | 790 | 680 | 46.03% |
| MCB traces | 0.280% | 0.265% | 0.255% | 0.242% | 13.57% |
| PCBSA traces | 2.800% | 2.700% | 2.570% | 2.490% | 11.07% |
| A.N.(ppm) | 4220 | 3750 | 2700 | 2280 | 45.97% |

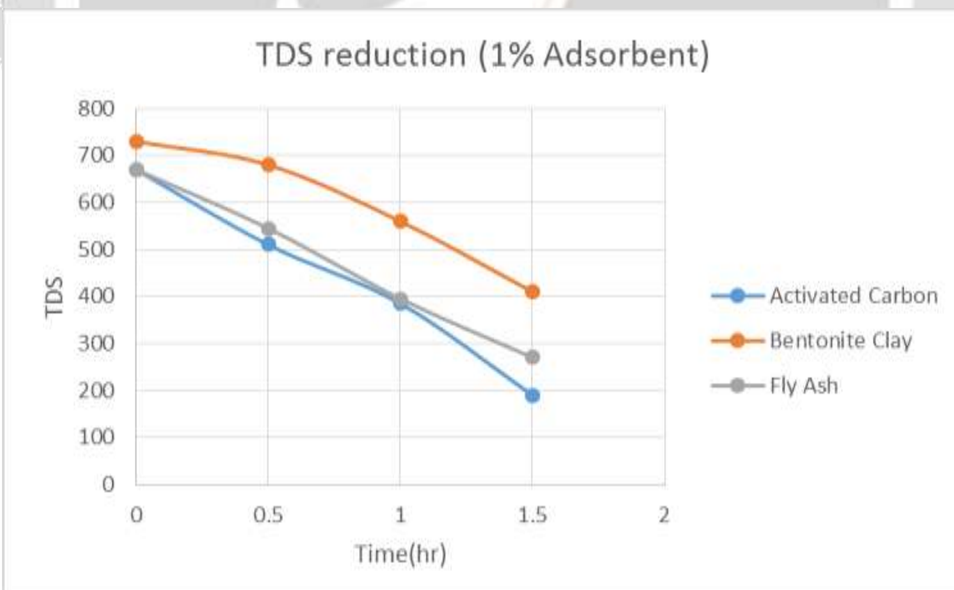
**4.1 Comparison Charts:-**

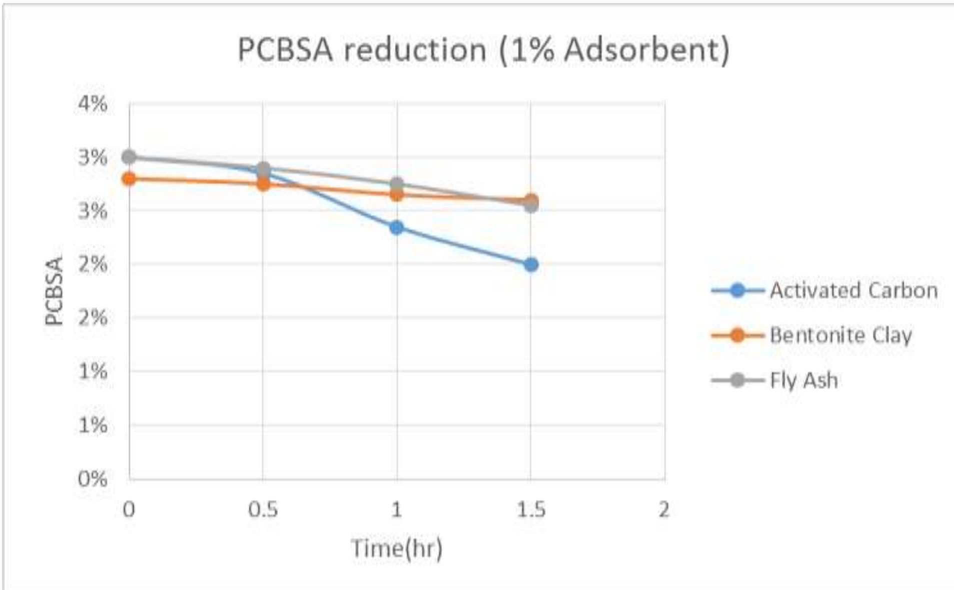


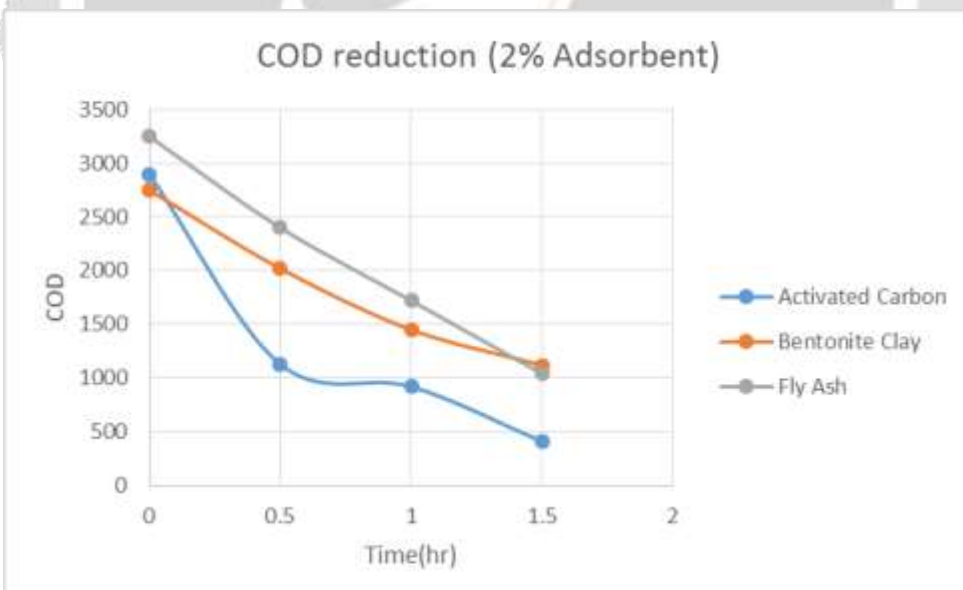

BOD reduction (1% Adsorbent)
BOD
1800
1600
1400
1200
1000
800
600
400
200
0
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash

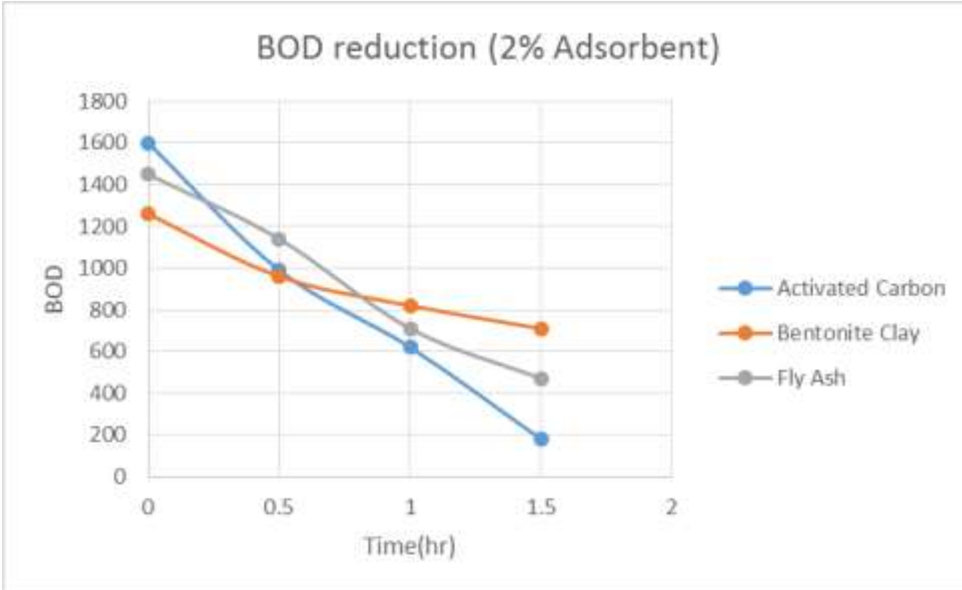

A.N. reduction (1% Adsorbent)
A.N.
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash

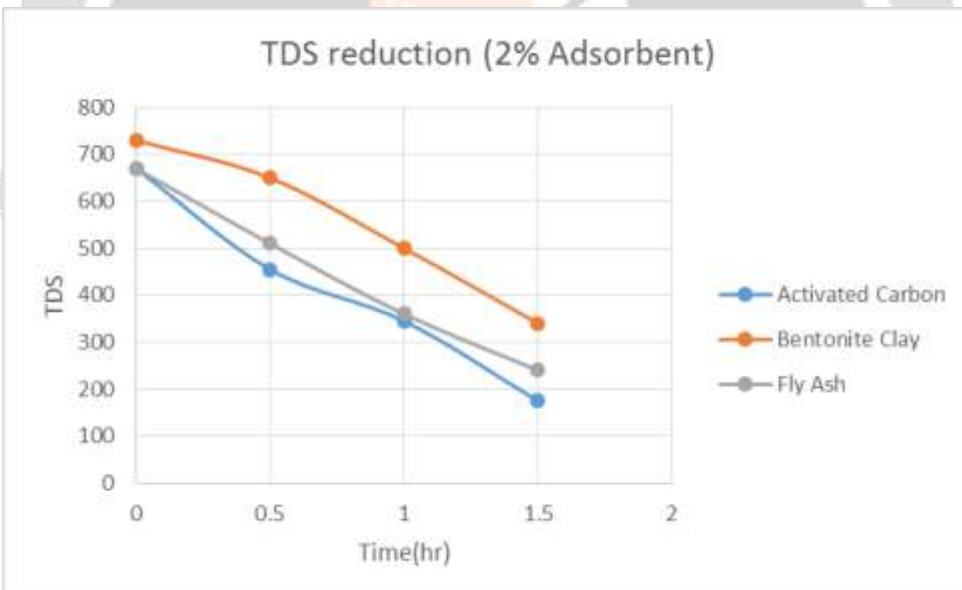

MCB reduction (1% Adsorbent)
0.35%
0.30%
0.25%
0.20%
0.15%
0.10%
0.05%
0.00%
MCB
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash

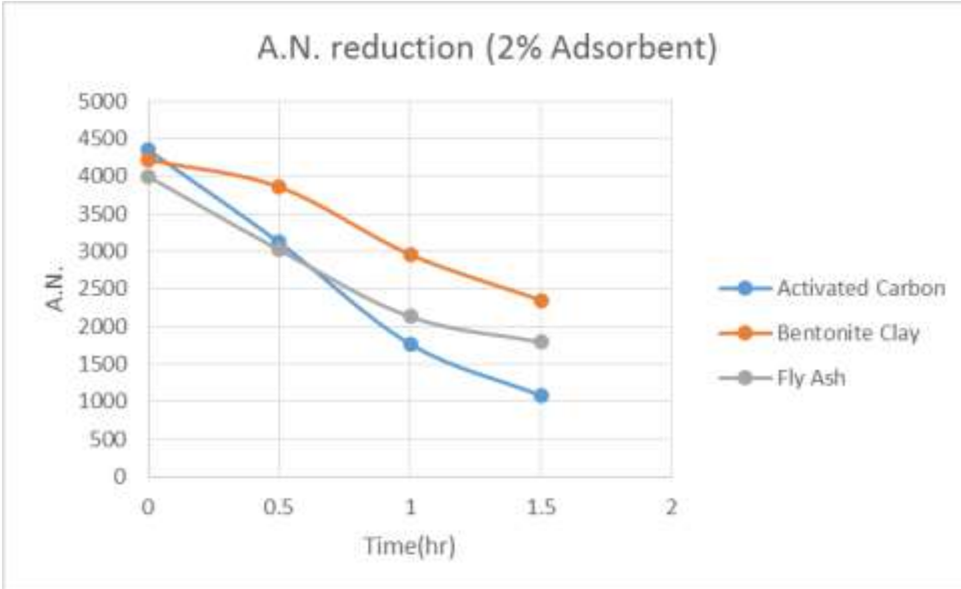

TDS reduction (1% Adsorbent)
800
700
600
500
400
300
200
100
0
TDS
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash

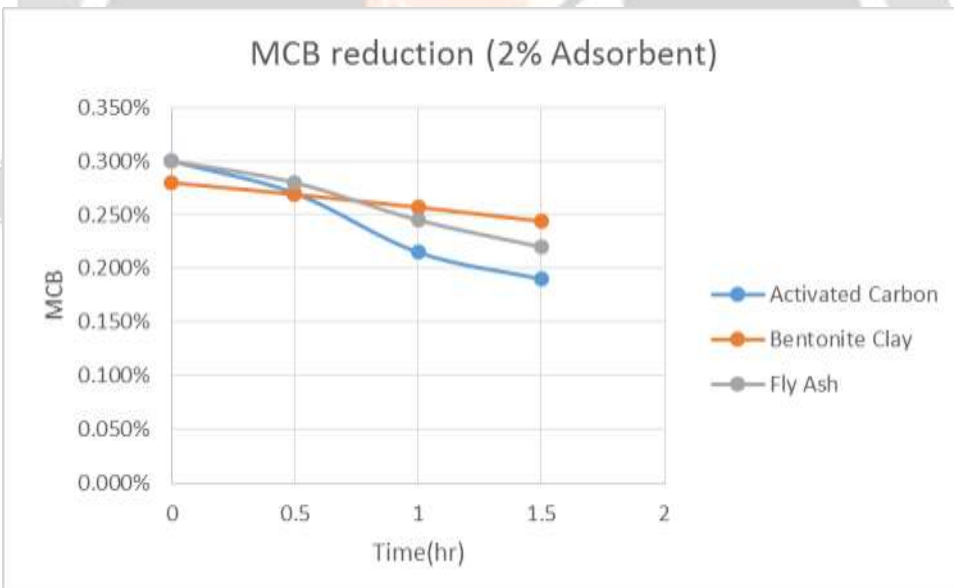

PCBSA reduction (1% Adsorbent)
PCBSA
Time(hr)
4%
3%
3%
2%
2%
1%
1%
0%
0
0.5
1
1.5
2
Activated Carbon
Bentonite Clay
Fly Ash

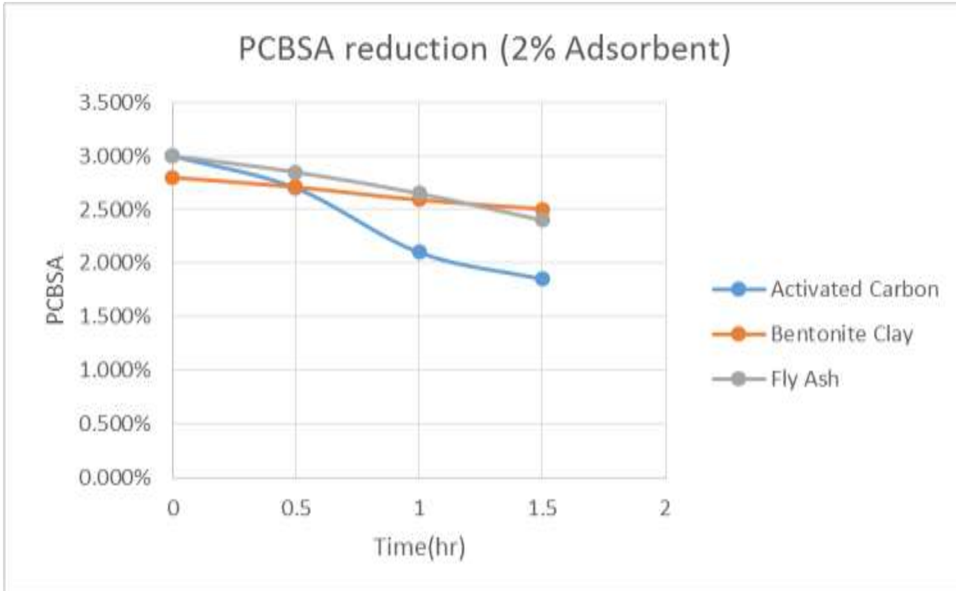

COD reduction (2% Adsorbent)
COD
Time(hr)
3500
3000
2500
2000
1500
1000
500
0
0
0.5
1
1.5
2
Activated Carbon
Bentonite Clay
Fly Ash

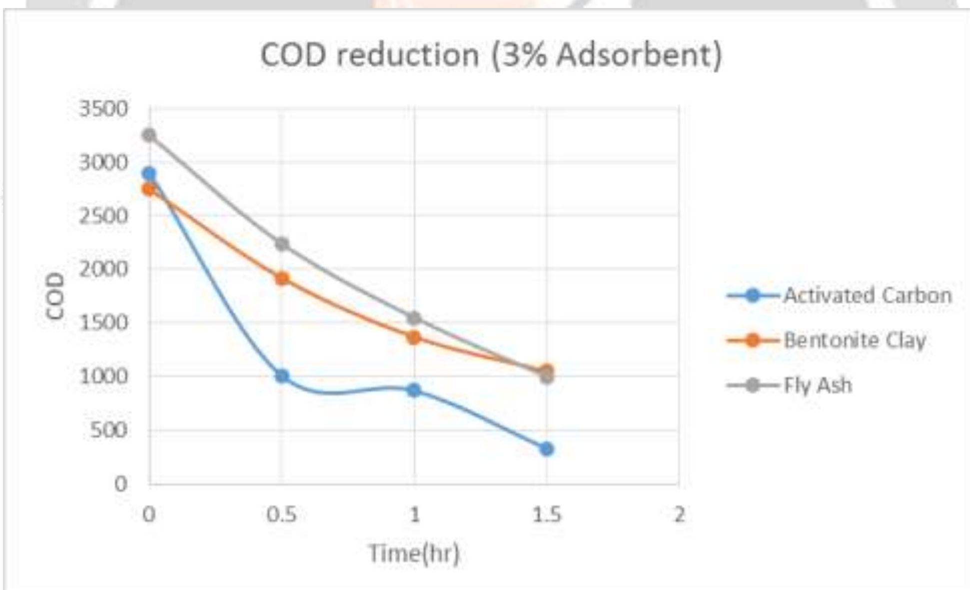

BOD reduction (2% Adsorbent)
BOD
1800
1600
1400
1200
1000
800
600
400
200
0
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash

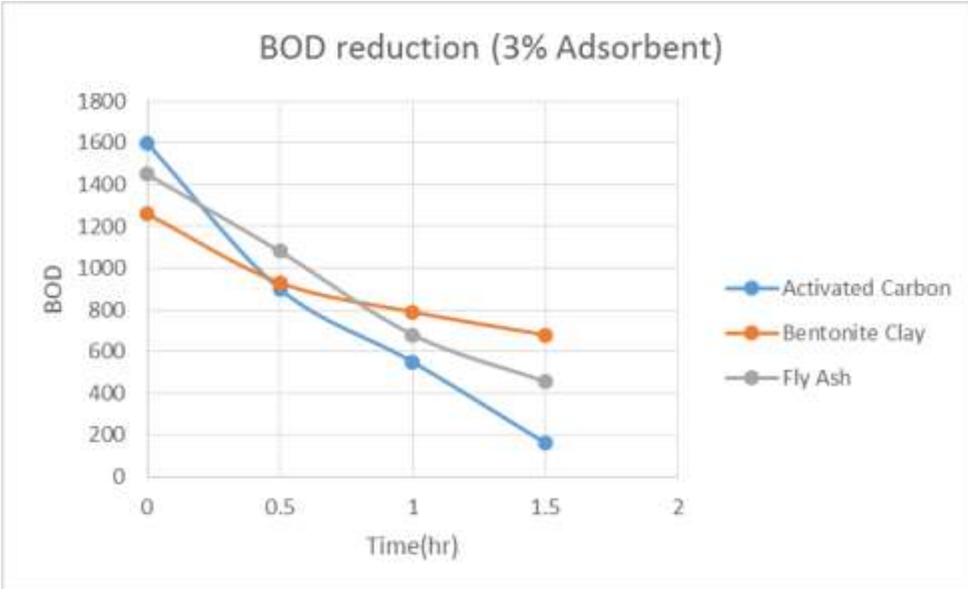

TDS reduction (2% Adsorbent)
TDS
800
700
600
500
400
300
200
100
0
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash

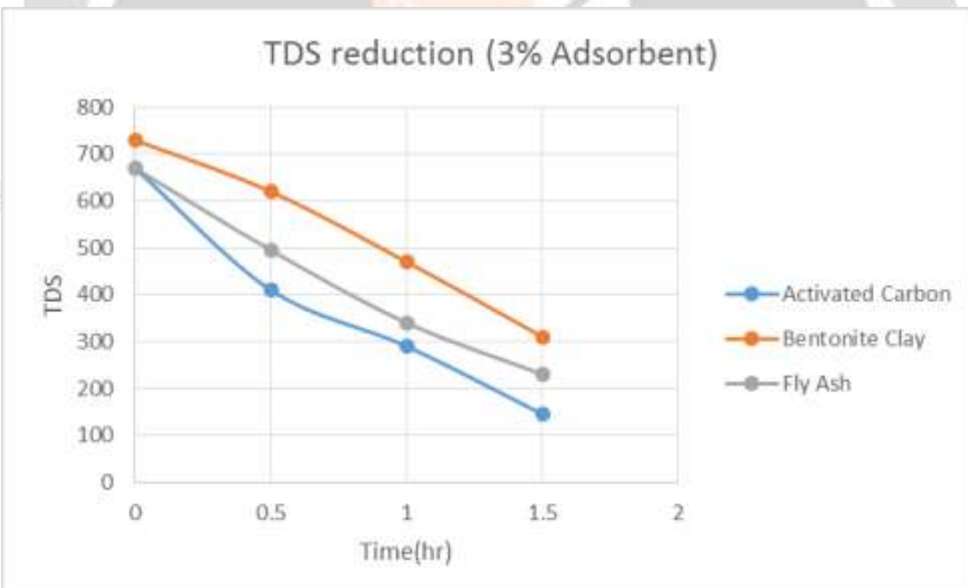

A.N. reduction (2% Adsorbent)
A.N.
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash

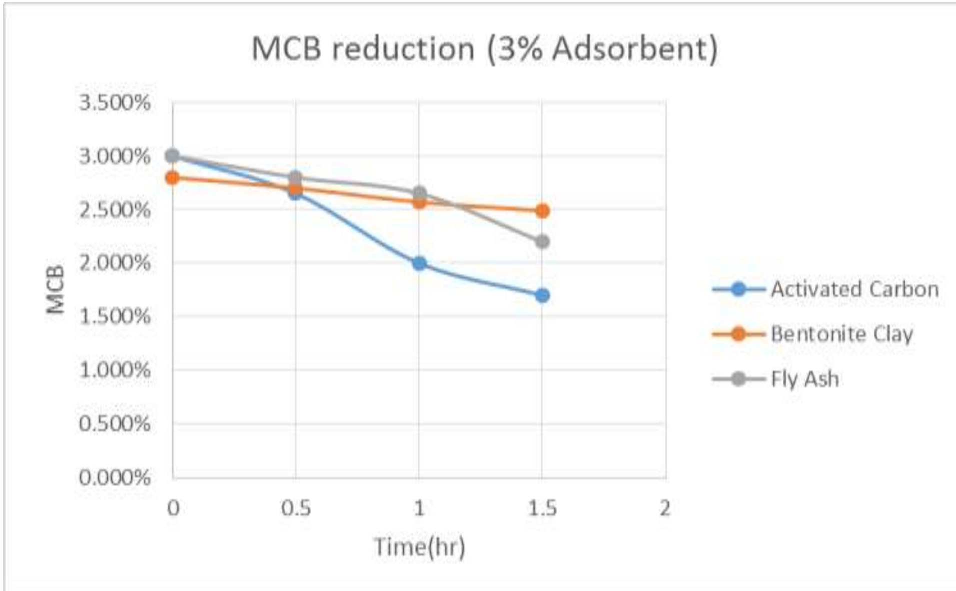

MCB reduction (2% Adsorbent)
MCB
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash

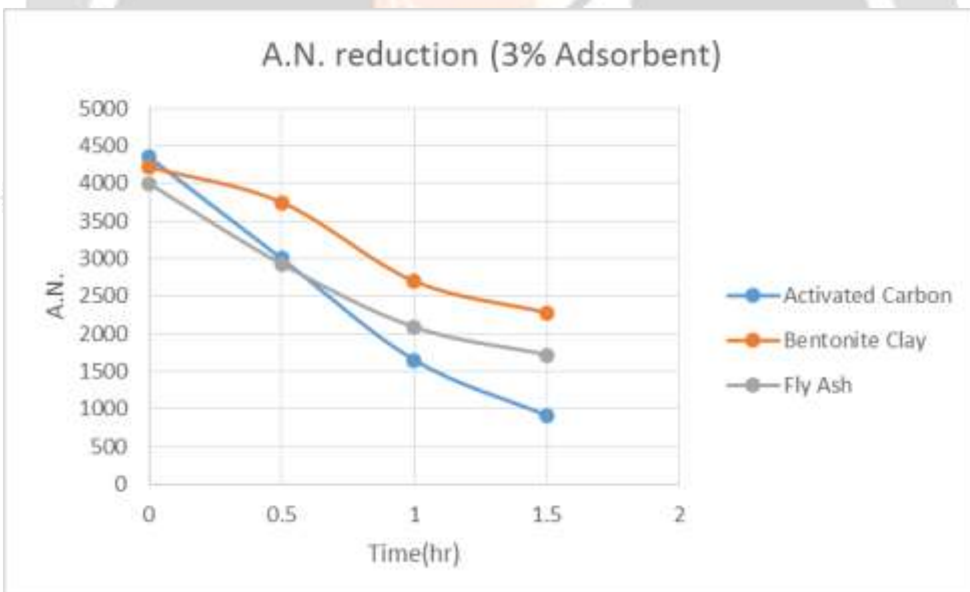

PCBSA reduction (2% Adsorbent)
3.500%
3.000%
2.500%
2.000%
1.500%
1.000%
0.500%
0.000%
PCBSA
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash

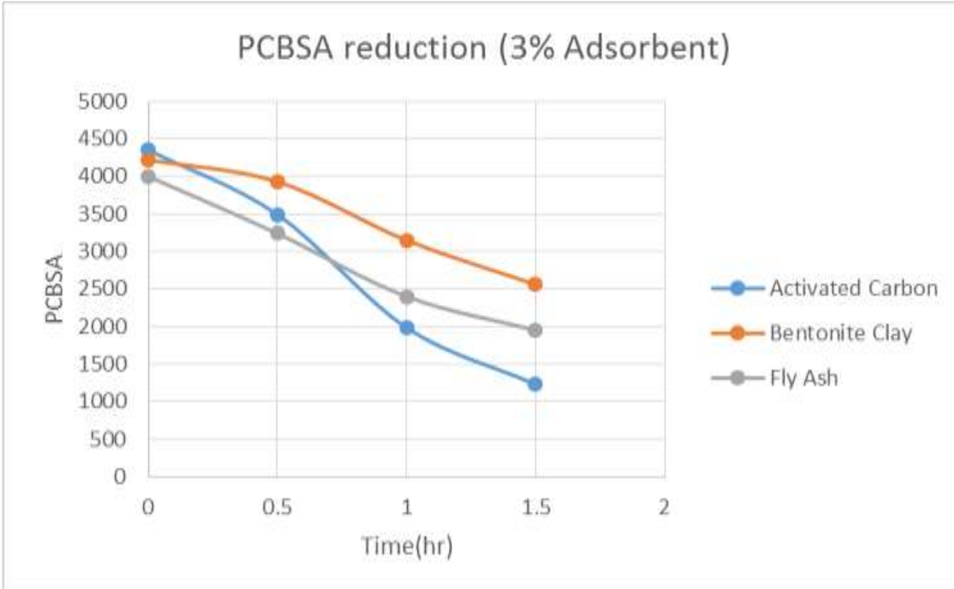

COD reduction (3% Adsorbent)
3500
3000
2500
2000
1500
1000
500
0
COD
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash


BOD reduction (3% Adsorbent)
BOD
1800
1600
1400
1200
1000
800
600
400
200
0
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash


TDS reduction (3% Adsorbent)
TDS
800
700
600
500
400
300
200
100
0
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash


MCB reduction (3% Adsorbent)
3.500%
3.000%
2.500%
2.000%
1.500%
1.000%
0.500%
0.000%
MCB
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash


A.N. reduction (3% Adsorbent)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
A.N.
0
0.5
1
1.5
2
Time(hr)
Activated Carbon
Bentonite Clay
Fly Ash




## 5. CONCLUSIONS:-

- From the above graphs and result tables, activated carbon is the most effective for the removal of the impurities to some extent.
- Fly ash gives good results in the removal of the impurities in comparison with bentonite clay.
- As the adsorbent dosage is increased from 1% to 2%, the removal of the impurities increases up to 10% for each impurities.
- Further increasing in the adsorbent dosage gives only 1-4% of excess removal of impurities only.
- Permissible limit of MCB and PCBSA in the waste water is 0 ppm so this treated water sample has to be sent for the further treatment to remove this two impurities completely.

## 6. ACKNOWLEDGEMENT:-

I am very much thankful to Vishwakarma Government Engineering College and Prof. N. M. Patel for their guidance and support. I am also very much thankful to Mr. Mitesh Dhimmar and Rachana Solanki, Nilam Patel and Dhaval Patel for providing services and support.

## 7. REFERENCES:-

[1]. C. Namasivayam and K. Ranganathan, “Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater,” Environmental Pollution, vol. 82, no. 3, pp. 255–261, Jan. 1993.

[2]. T. S. Anirudhan and P. S. Suchithra, “Humic acid-immobilized polymer/bentonite composite as an adsorbent for the removal of copper(II) ions from aqueous solutions and electroplating industry wastewater,” Journal of Industrial and Engineering Chemistry, vol. 16, no. 1, pp. 130–139, Jan. 2010.

[3]. Y.Wu et al., “Functionalized agricultural biomass as a low-cost adsorbent: Utilization of rice straw incorporated with amine groups for the adsorption of Cr(VI) and Ni(II) from single and binary systems,” Biochemical Engineering Journal, vol. 105, pp. 27–35, Jan. 2016.

[4]. I. Alomá, M. A. Martín-Lara, I. L. Rodríguez, G. Blázquez, and M. Calero, “Removal of nickel (II) ions from aqueous solutions by biosorption on sugarcane bagasse,” Journal of the Taiwan Institute of Chemical Engineers, vol. 43, no. 2, pp. 275–281,Mar. 2012.

[5]. T. A. H. Nguyen et al., “Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater,” Bioresource Technology, vol. 148, pp. 574–585, Nov. 2013.

[6]. W. S. Wan Ngah and M. A. K. M. Hanafiah, “Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review,” Bioresource Technology, vol. 99, no. 10, pp. 3935–3948, Jul. 2008.

[7]. R. Sivaraj, C. Namasivayam, and K. Kadirvelu, “Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions,” Waste management, vol. 21, no. 1, pp. 105–110, 2001.

[8]. A. K. Zeraatkar, H. Ahmadzadeh, A. F. Talebi,N. R.Moheimani, and M. P.McHenry, “Potential use of algae for heavy metal bioremediation, a critical review,” Journal of Environmental Management, vol. 181, pp. 817–831, Oct. 2016.

[9]. R. N. Coimbra, V. Calisto, C. I. A. Ferreira, V. I. Esteves, and M. Otero, “Removal of pharmaceuticals from municipal wastewater by adsorption onto pyrolyzed pulp mill sludge,” Arabian Journal of Chemistry.