IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

COD Reduction Using Modified Effluent Treatment Flowsheet for Waste Water Generated During Production of 4, 4'-Diaminostilbene- 2, 2'-Disulfonic Acid

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Abstract

The manufacturing process of DASDA (4, 4'-Diaminostilbene- 2, 2'-disulfonic Acid) is conventionally carried out mainly by Sulfonation followed by Oxidation and Reduction. In this process iron powder and hydrochloric acid produces large quantity of solid ferrous chloride which is hazardous solid waste which creates a problem during the waste water treatment. After oxidation is carried out the filtrate contains 1.2- 1.5% DNSDA (4, 4'-dinitrostilbene 2, 2' – disulphonic acid) which goes along with the waste water stream to effluent treatment plant and increases COD level. The cost of treatment of effluent to decrease the COD adds up to cost of production. Moreover, time required for treatment also slows down the production.

As there is no replacement of this process one can either recover DNSDA or nullify its effect before COD increases in the effluent stream. Here experiments have been carried out and it has been shown that how cheap adsorbents such as activated carbon and lignite powder can drastically decrease the COD levels. With a change in conventional effluent treatment flowsheet the COD is reduced substantially at the first stage facilitating further treatment. These results will help all the small and medium scale industries as adsorbents used are cheap and no major change is required in present equipment setup. We are trying to approach a cleaner production method which is more suitable method in order to get a clean manufacturing process with reduced waste.

Keywords : COD removal, low cost adsorbents DASDA, cleaner production approach, modified effluent treatment flowsheet.

Introduction

The term Cleaner Production was defined by UNEP (United Nations Environment Program) in 1990 as: "The continuous application of an integrated environmental strategy to processes, products and services to increase efficiency and reduce risks to humans and the environment". This definition has been used as the working definition of all programmers related to the promotion of cleaner production and still continues to be a valid definition.

Cleaner Production Principles:-

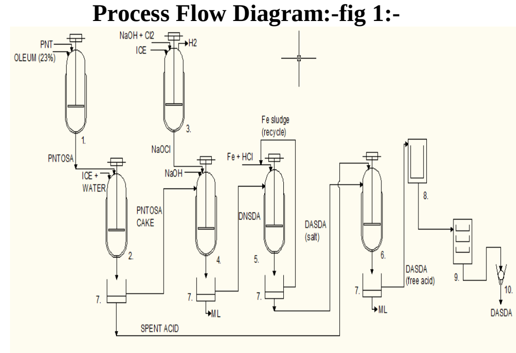
1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthesis methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feed stock should be renewable rather than depleting whenever technically and economically practical.
8. Unnecessary derivatization (blocking group, protection/deprotection, and temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products would be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. Substances and formation of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

DASDA Manufacturing Process

1. **Sulphonation** :-
   Take 1000 kgs PNT in close lead reactor while stirring continuously. Now slowly add 2500 to 2700 kgs oleum (23 %) by continuously maintaining the temperature 95 ^{0}c to 100 ^{0}c. When oleum additions is over then check mass with PNT test, if it is ok start cooling up to room temperature then filter it out. The product is called PNTOSA and mother liquor is spent acid.
2. **Dumping and Filtration:-**
   The sulfomass formed is dumped at controlled rate. The whole sulfomass is dumped in 2 lots. Each lot takes 12 – 14 hrs and temperature is maintained 50^{0}c. After dumping is over, mass is pumped to nutsche filter. The filtrate known as spent acid is collected in a tank. The same is used in isolation process and remaining is commercially sellable. The filtration operation takes about 3 to 4 hrs. Cake obtained is PNTOSA, which is then centrifuged and sent for further process in oxidation vessel.
3. **Chlorination**:-
   Take 1200 kgs (100%) NaOH in hypo manufacturing tank and add 900 kgs ice and slowly charge 600 kgs chlorine. During this reaction temperature is maintained below 10^{0}c by ice to make pH 7 to 7.5.
4. **Oxidation**:-
   Take about 10000 lit of tap water in brick lined vessel, heat upto 90^{0}c and add previously obtained PNTOSA. Make solution neutral by adding 600 kgs of soda ash. Now slowly add prepared hypo chloride solution. At this time add 300 to 400 kgs NaOH (100%). When hypo charging is over then add 10% salt of total volume, cool it down to room temperature and filter out by nutsche. Collect mass as DNSDA and mother liquor run out in ETP.
5. **Reduction**:-
   Take approximately 10000 lit tap water in reduction tank and heat it up to 95^{0}c temperature. Now add 650 to 700 kgs iron powder (Fe) and add HCl to adjust pH to 2. Start stirring and addition of above collected DNSDA. When reductions are completely over then add 40 to650 kgs of NaOH (100%). Filter out to clarify. Take, filtrate and transfer it to isolation tank.
6. Separation of Dasda:-
   The whole slurry from the reduction vessel is pumped to a plate and frame filter press. The filtrate is DASDA, which is taken to isolation vessel. The iron sludge is further washed with steam to remove maximum amount of DASDA.
7. **Isolation**:-
   Take above reduction filter mass and slowly charge spent acid to CR+ve (congo red test). There should be continuous stirring. By circulating steam the temperature of the reaction mass is brought up to 70^{0}c. Then filter out the mass by filter press. This product is DASDA.
8. **Filtration**:-
   After isolation the whole mass is then passed through the filter press. The cake from filter press is then sent to centrifuge and filtrate liquor goes to ETP.
9. **Centrifuge And Drying**:-
   After the filtration is over the cake is centrifuged and then centrifuged mass is filled in the tray for drying. The dried mass is then sent to pulveriser. Product as per requirement in cake form from centrifuge or powder form after drying is sent for packaging.

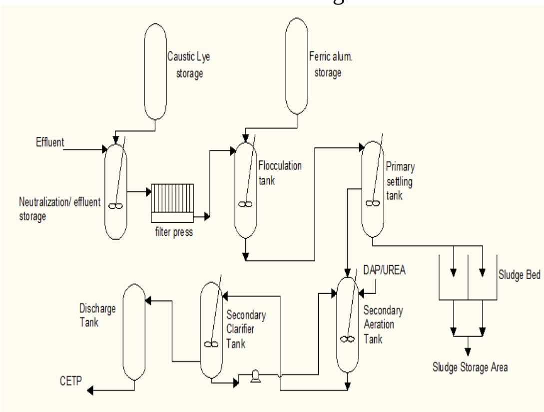
Process Flow Diagram:-fig 1:-



Sr. No.	Unit operation/Process
1.	Sulphonation
2.	Dumping
3.	Chlorination
4.	Oxidation
5.	Reduction
6.	Isolation
7.	Nutche filter/filter press
8.	Centrifuge
9.	Tray Dryer
10.	Pulveriser

 ISSN: 2277-9655

ETP:-fig 2:-



The Effluent Treatment Plant (ETP) is shown in above figure. First the effluents from all stages are collected in a storage/neutralization tank where caustic lye is added for neutralization.
After neutralization the stream is passed through filter press to remove solids and passed to the flocculation tank.

In the flocculation tank Ferric alum is added as a flocculating agent.

After flocculation the mass is transferred to primary settling tank where sludge is separated to sludge-bed which is then sent to sludge storage area.
The liquid from primary settling tank is sent to secondary aeration tank where DAP/Urea is added to decrease the COD level.

The mass is transferred to the secondary clarifier tank for further aeration to decrease the COD level.

After secondary clarifier tank if the COD level does not decrease then the mass is transferred again to the aeration tank where it is treated again with DAP/Urea.

Once the COD level goes bellow GPCB norms i.e., below 3000, it is stored in discharge tank and sent to CETP for further treatment.

The inlet stream of ETP has COD level ranging from 9000 – 10000 mg/lit, while after treatment in the ETP COD level comes to range of 6000 – 7000 mg/lit. So, to bring COD level below 3000 mg/lit re-treatment is done before sending to CETP.

Methodology

The conventional flow sheet of waste water treatment used by mist of the industrial units includes primary treatment, followed by secondary and tertiary treatments. During primary treatment, neutralization of the wastewater results in to increase of salts. Salts in high concentration inhibit biological activity and may cause an increase in nonsettleable suspended solids in the treated wastewater. The flow sheet given subsequently is therefore proposed, wherein adsorption with inexpensive adsorbents could be employed, prior to the conventional primary treatment for increasing efficiency of the biological treatment.

Wastewater →	pH adjustment	→	Physicochemical/ Biological treatment	→	Adsorption	→	Treated Wastewater

This is expected to reduce refractory organics COD as well as BOD of the wastewater substantially at the first stage of wastewater treatment itself facilitating further treatment. From multi-stage production processes used in the production of organic chemicals, wastewater stream is likely to contain several organics as well as inorganic substances including products, intermediates, side products, by products and un-reacted raw materials.

Wastewater →	Adsorption	→	ph adjustment	→	Physicochemical/ Biological treatment	→	Treated Waste water

The industrial waste water being highly complex and varying widely in the absorbability of the compounds present the detailed analysis of such wastewater streams and study of their adsorption on different adsorbents was very complex. It was therefore decided to consider COD as the measured. These parameters COD and colour reflect the practical aspects of wastewater treatment on the industrial scale. Thus such a study should be of much relevance to the industry in selecting cost effective wastewater treatment technique for complying with the statutory regulations. The approach followed in the evaluation of adsorption performance of different adsorbents viz. Activated carbon, lignite in the treatment of waste water is thus based on detection of COD and colour in the wastewater with varying degree of treatment. This approach is entirely different from that followed by many of the researches who prepare wastewater samples from known solutes in the laboratory and carry out chemical analysis of the treated sample.

Experimental Procedure

For the contact time experiments, waste water sample from Dyes intermediate plant were collected in labelled carboys and the carboys were then sealed. The samples are of ETP inlet stream and

ETP outlet / CETP inlet stream. These samples were directly from the process plant streams before these had any chance of getting mixed with any other stream. In most of the cases these were concentrated streams, often referred as mother liquor. While carrying out experimental studies on the waste water from each carboy sample was analyzed for pH and COD. During experiment 200ml of sample is to be taken from the respective carboy in a cylindrical flask. In which 1% (2gm) Activated carbon (A/C) is to be added in to the flask and magnetic stirrer is started. 5-10 ml of sample is to be drawn in time interval of 10, 20, 30, 45, 60, 90, 120 min from this mass. Then Filtered on filter paper and the filtrate analyzed for COD. At the end of 2hr the stirring is stopped and the experiment is terminated. The experiments are to be repeated with 2% A/C, 3% A/C and 4% A/C, and similar procedure follow for Lignite adsorbent. All the experiments are to be carried out at room temperature of around 30°C.

Experimental observations: - Table 1:-

Sample (200ml) with 1 % activated carbon (2 gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*20	%COD reduction
0	10.5	7.8	0.255	8000	10	550.8	11016	0
10	10.5	8	0.255	8000	10	510	10200	7.40
20	10.5	8.2	0.255	8000	10	469.2	9384	14.81
30	10.5	8.3	0.255	8000	10	448.8	8976	18.51
40	10.5	8.4	0.255	8000	10	428.4	8568	22.22
50	10.5	8.5	0.255	8000	10	408	8160	25.92
60	10.5	8.5	0.255	8000	10	408	8160	25.92
90	10.5	8.8	0.255	8000	10	346.8	6936	37.03
120	10.5	8.9	0.255	8000	10	326.4	6528	40.74

Fig 2:-

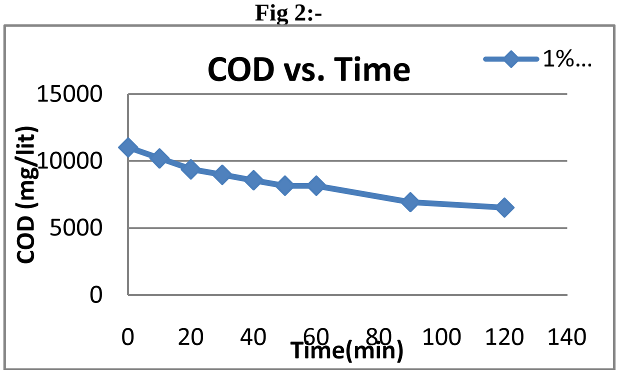


Fig 3:-

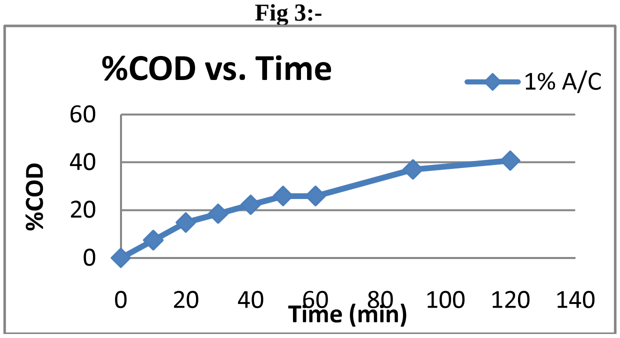


Table 2:-

Sample (200ml) with 2 % activated carbon (4 gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*20	%COD reduction
0	10.4	7.8	0.255	8000	10	530.4	10608	0
10	10.4	8.1	0.255	8000	10	469.2	9384	11.53
20	10.4	8.2	0.255	8000	10	448.8	8976	15.38
30	10.4	8.4	0.255	8000	10	408	8160	23.07
40	10.4	8.5	0.255	8000	10	387.6	7752	26.92
50	10.4	8.6	0.255	8000	10	367.2	7344	30.76
60	10.4	8.7	0.255	8000	10	346.8	6936	34.61
90	10.4	9	0.255	8000	10	285.6	5712	46.15
120	10.4	9.2	0.255	8000	10	244.8	4896	53.84

Fig 4:-

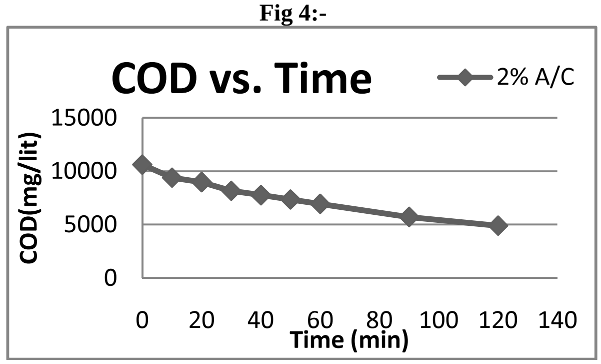


Fig 5:-

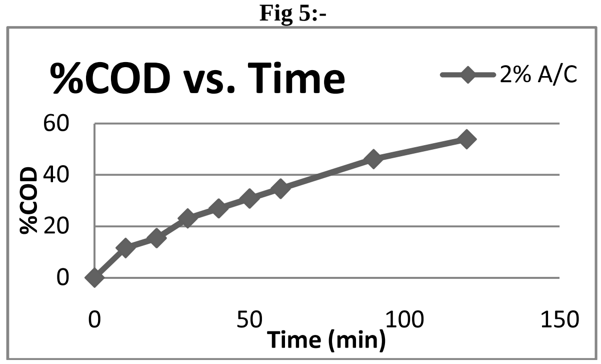


Table 3:-

Sample (200ml) with 3 % activated carbon (6 gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*20	%COD reduction
0	10.6	8.1	0.255	8000	10	510	10200	0
10	10.6	8.4	0.255	8000	10	448.8	8976	12
20	10.6	8.6	0.255	8000	10	408	8160	20
30	10.6	8.7	0.255	8000	10	387.6	7752	24
40	10.6	8.9	0.255	8000	10	346.8	6936	32
50	10.6	9	0.255	8000	10	326.4	6528	36
60	10.6	9.1	0.255	8000	10	306	6120	40
90	10.6	9.4	0.255	8000	10	244.8	4896	52
120	10.6	9.6	0.255	8000	10	204	4080	60

 ISSN: 2277-9655

Fig 6:-

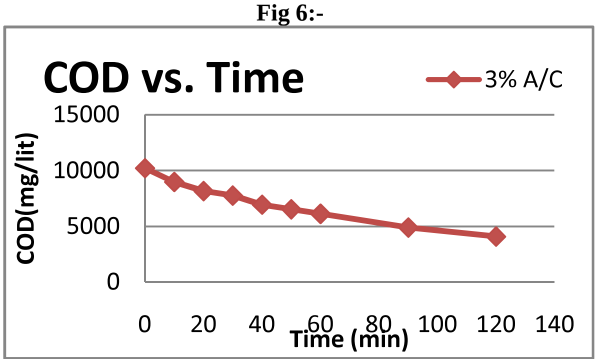


Fig 7:-

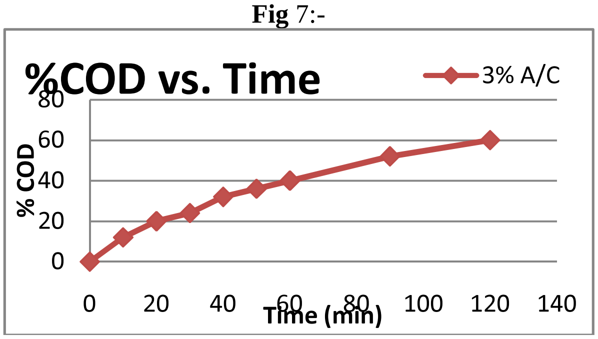


Table 4:-

Sample (200ml) with 4 % activated carbon (8 gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*20	%COD reduction
0	10.6	8.1	0.255	8000	10	510	10200	0
10	10.6	8.6	0.255	8000	10	408	8160	20
20	10.6	8.8	0.255	8000	10	367.2	7344	28
30	10.6	9	0.255	8000	10	326.4	6528	36
40	10.6	9.1	0.255	8000	10	306	6120	40
50	10.6	9.3	0.255	8000	10	265.2	5304	48
60	10.6	9.4	0.255	8000	10	244.8	4896	52
90	10.6	9.7	0.255	8000	10	183.6	3672	64
120	10.6	9.9	0.255	8000	10	142.8	2856	72

Fig 8:-

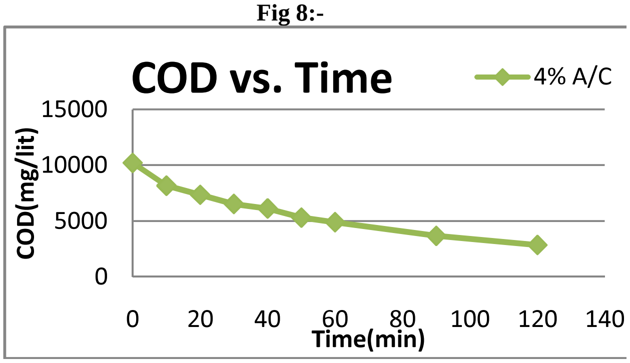


Fig 9:-

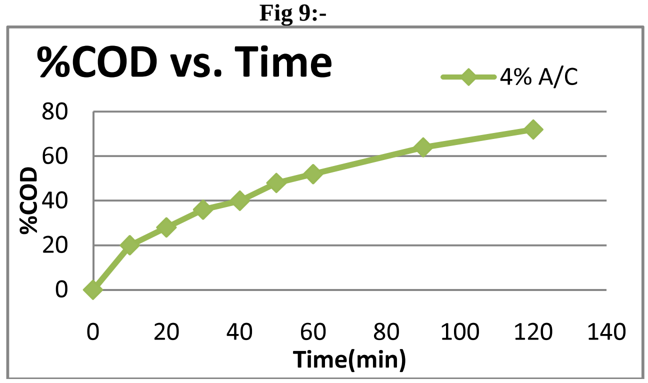


Table 5:-

Sample (200ml) with 1% Lignite powder (2 gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*20	%COD reduction
0	11.2	8.7	0.255	8000	10	510	10200	0
10	11.2	8.9	0.255	8000	10	469.2	9384	8
20	11.2	9.2	0.255	8000	10	408	8160	20
30	11.2	9.4	0.255	8000	10	367.2	7344	28
40	11.2	9.5	0.255	8000	10	346.8	6936	32
50	11.2	9.8	0.255	8000	10	285.6	5712	44
60	11.2	9.9	0.255	8000	10	265.2	5304	48
90	11.2	10.1	0.255	8000	10	224.4	4488	56
120	11.2	10.3	0.255	8000	10	183.6	3672	64

Fig 10:-

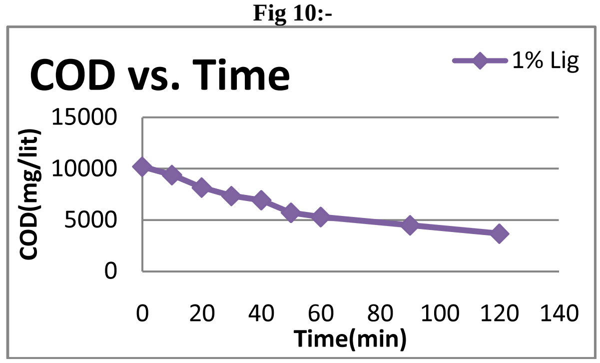


Fig 11:-

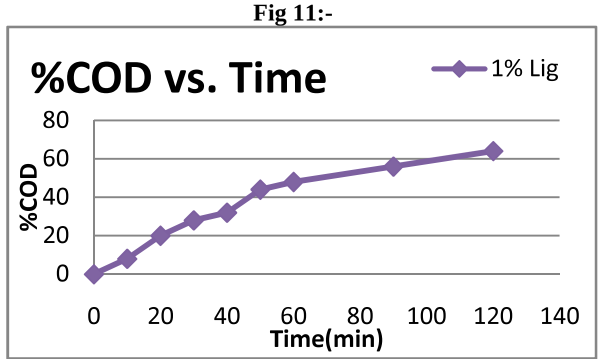


Table 6:-

Sample (200ml) with 2% Lignite powder (4 gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*20	%COD reduction
0	11	8.5	0.255	8000	10	510	10200	0
10	11	8.8	0.255	8000	10	448.8	8976	12
20	11	9.1	0.255	8000	10	387.6	7752	24
30	11	9.3	0.255	8000	10	346.8	6936	32
40	11	9.5	0.255	8000	10	306	6120	40
50	11	9.8	0.255	8000	10	244.8	4896	52
60	11	9.9	0.255	8000	10	224.4	4488	56
90	11	10.1	0.255	8000	10	183.6	3672	64
120	11	10.3	0.255	8000	10	142.8	2856	72

Fig 12:-

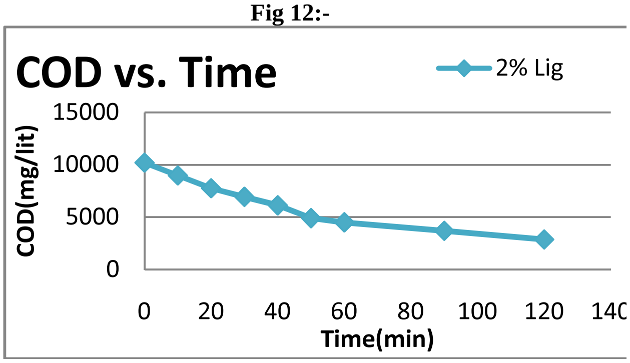


Fig 13:-

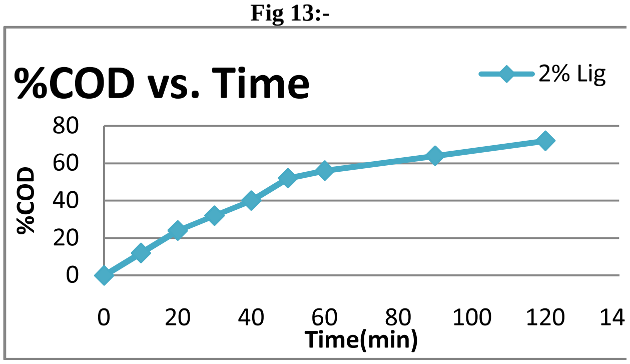


Table 7:-

Sample (200ml) with 3% Lignite powder (6 gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*20	%COI reducti
0	10.7	8.22	0.255	8000	10	505.92	10118.4	
10	10.7	8.7	0.255	8000	10	408	8160	19.
20	10.7	8.9	0.255	8000	10	367.2	7344	27.
30	10.7	9.1	0.255	8000	10	326.4	6528	35.
40	10.7	9.4	0.255	8000	10	265.2	5304	47.
50	10.7	9.7	0.255	8000	10	204	4080	59.
60	10.7	9.84	0.255	8000	10	175.44	3508.8	65.
90	10.7	10.1	0.255	8000	10	122.4	2448	75.
120	10.7	10.3	0.255	8000	10	81.6	1632	83.

Fig 14:-

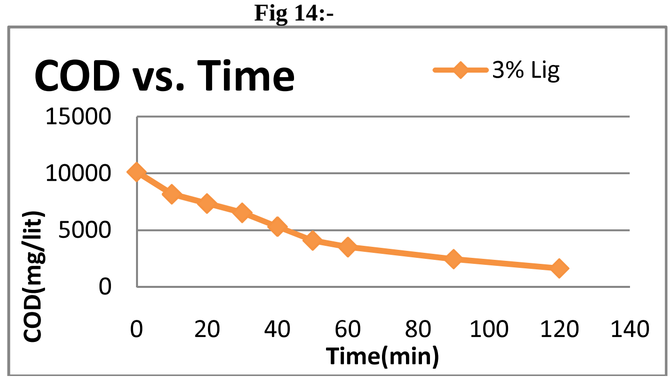
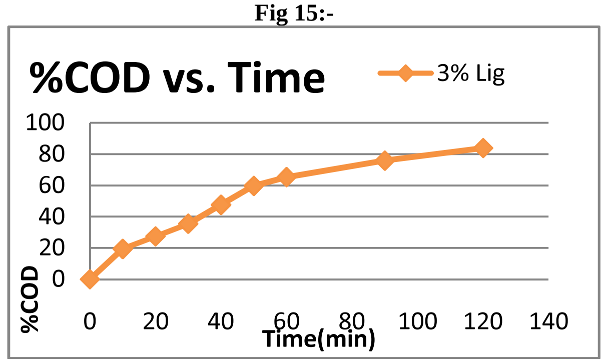


Fig 15:-



Conclusion

When we compare these results with conventional Effluent Treatment Plant the efficiency to decrease the COD is increased. Based on this modified effluent treatment flowsheet one can save energy as well as time for treatment of effluent and cost of production decreases.The adsorbents activated carbon and lignite powder are cheap and easily available so small and medium scale industries can easily use these methodology.

From the above mentioned experimental observations and corresponding graphs it is clear that percentage of COD reduction is maximum for adsorption with 3 % lignite powder, which is 83.87 % in 2 hours. These reduction obtained is sufficient and thus one can filter the effluent and discard to CETP. Thus, COD can be reduced using a modified effluent treatment flowsheet by using adsorption with lignite powder for treatment of waste water generated during the production of 4, 4'-Diaminostilbene- 2, 2'-disulfonic Acid.

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