

COD reduction using modifying industrial effluent treatment flowsheet and low cost adsorbent as a part of cleaner production

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ABSTRACT

Modern environmental legislation is becoming much more internationally coherent and less prescriptive, and focused on prevention of pollution through control of hazardous materials and processes as well as on protection of eco-systems. Active Pharmaceutical Intermediates from waste water streams of API companies are emerging contaminants in the aquatic environment, because of their adverse effect on aquatic life and humans. These contaminants are high in COD and difficult to treat biologically. A number of technologies have been developed over the years to remove organic matter from industrial wastewater. The most important technologies include coagulation/flocculation process, membrane filtration, and oxidation process. These methods are generally expensive, complicated, time consuming and requires skilled personnel. The high cost of coal-based activated carbons has stimulated the search for cheaper alternatives. Low cost and non-conventional adsorbents like activated carbon, Lignite, Fly ash, Neem tree leaves are used as a adsorbents for removing COD of Industrial waste water. Activated carbon is a commonly used adsorbent in sugar refining, chemical and pharmaceutical industries, and water and wastewater treatment. Increasing requirements for clearer and more polished effluent from many processes suggest that, barring the development of new technologies, industrial need for activated carbon will only increase in future. Fly ash has shown quite effective adsorbent capacity for COD reduction from the Industrial wastewater. Though its capacity is lower than that of commercial grade activated carbon, the low material cost makes it an attractive option for the treatment of Industrial waste water which contains phenolic compounds. The study aims at demonstrating that adsorption as the first stage of treatment increases efficiency of the subsequent biological treatment. Experiments are carried out on different wastewater samples from chemical plants on adsorbents viz. activated carbon, bentonite, and lignite. The effectiveness of adsorbents in the removal of refractory organics by way of reducing chemical oxygen demand and colour is evaluated. The results of COD reduction are fitted into different models available in literature including the new model Rathi Puranik equation, which requires least experimentation for predicting COD values

Keywords: Adsorption efficiency, low cost adsorbents, Rathi-Puranik model, Phenolic compound, COD removal.

INTRODUCTION

Cleaner production

The primary function of the economic activities is to process input resources (raw materials, energy, water, etc.) into usable outputs. However all the inputs are not transformed into products? The portion that does not get transformed into useful outputs comes out as wastes. This transformation into waste depends on the technology employed and efficiency of the process.

Since the 1960's, mostly, problems with emissions of pollutants from industrial sources to the environment were addressed by the utilization of end of pipe (EOP) pollution control technologies. These approaches reduced the direct release of some pollutants to achieve regulatory compliance but did not really solve the problems. Often, the

pollutants were only transferred from one sink to the other. Additionally, end-of-pipe treatment is very cost intensive with huge operation and maintenance charges.

Since 1972, pollution control patterns have begun to change. During the 1970s and 1980s, various concepts and strategies emerged, such as minimization of wastes, source reduction instead of end-of-pipe treatment, pollution prevention, and “no or less” waste generation process.

Cleaner Production (CP) on the contrary is a common sense approach: Instead of treating waste and emissions in end-of-pipe treatment plants, we try to define ways to prevent the production of the pollutants. This approach includes organizational changes, motivation and training for good housekeeping as well as changes in raw materials, process technology, internal and external recycling.

CP Concept

Cleaner production is a pro-active and integrated solution to pollution problems by eliminating or reducing pollutants at the source during the course of production processes. Cleaner production, with great vitality and buoyancy, begins a new era of “Pollution Prevention” in the history of environmental protection and will become the best approach for pollution control in this new century.

Cleaner Production concepts have consequences for the whole life cycle of a product and can foster improvements in product design, selection of raw materials, efficiency in production and energy usage, safety during manufacture and consumer use, reparability, and recyclables.

More specifically, Cleaner production aims to reduce the consumption of natural resources per unit of production, the amount of pollutants generated, and their environmental impact, while making alternative products and processes financially and politically more attractive. As the European Environmental Agency states, “*Cleaner Production is about the creation of a truly sustainable economy*”. Cleaner Production brings economic benefits via increased resource efficiency, innovation and reduction.

What is Cleaner Production?

Cleaner Production can be defined as: A new and creative way of thinking about products and the processes that makes them. It is achieved by the continuous application of strategies to minimize the generation of wastes and emissions.

Cleaner Production means improvements to a production process do the process uses less energy, water or other input, or generates less waste or less environmentally harmful waste.

Cleaner Production means increasing production efficiency while at the same time minimizing waste and the pollution of our environment.

UNEP Definition of Cleaner Production:

“Cleaner Production means the continuous application of an integrated preventive environmental strategy to processes and products to reduce risks to humans and the environment”.

“*Cleaner Production is a forward-looking, ‘anticipate and prevent’ philosophy*”.

Paracetamol is one of the most common drugs used in the world, and is manufactured in huge quantities. Paracetamol was first synthesised by Morse in 1878 by the reduction of p-nitrophenol with tin in glacial acetic acid. The p-aminophenol produced by the reducing action of the tin was acetylated in situ by the acetic acid.

Paracetamol (acetaminophen, *N*-(4-hydroxyphenyl) acetamide) has analgesic and antipyretic properties, but no relevant anti-inflammatory action. It is used for the treatment of various mild to moderate pain conditions and to reduce fever. Despite a long therapeutic use, the mechanism of action of paracetamol is unclear. Paracetamol is one of the most popular analgesics as single drug or in multi-ingredient preparations, often in combination with weak opioids.

Routes available for production of Paracetamol:

Being an important pharmaceutical product (drug), paracetamol can be manufactured by different routes. World over, the following four routes have been established for the manufacture of Paracetamol:

- Phenol Route
- Para Nitrochloro Benzene (PNCB) Route

p-Nitrophenol is reduced with iron at 90-100°C temperature in wooden vat. The reaction temperature is raised by direct injection of steam. On completion of reduction, water is added to the reaction mass, iron sludge is removed by filtration and the filtrate is cooled to 15°C p-Aminophenol is filtered and the filtrate is collected. This filtrate, containing p-aminophenol could be re-used in the reduction step 4-5 times before being discharged as effluent. Proper design of the reduction vessel along with optimum stirring speed should also result in the improvement of the yields. The iron sludge could be used for making iron oxide for red oxide primers. Catalytic hydrogenation or electrolytic reduction of p-nitrophenol is likely to give higher yields and avoid solid wastes. Hydrogen transfer catalysis is likely to give all these advantages, without handling hydrogen gas. Pure p-aminophenol is reported to be prepared by adding more p-nitrophenol to the reaction mixture (if the reaction has gone to completion), adjusting the pH between 5.0 and 6.5 and separating the p-nitrophenol phase and the p-aminophenol could be purified by giving treatment with carbon in aqueous hydrochloric acid solution and it could be stabilized by the addition of sodium sulphite.

The acetylation of p-aminophenol to crude paracetamol is carried out by the addition of acetic anhydride. No attempt is made to control the temperature of this exothermic reaction. The temperature could increase to around 80°C. After cooling, crude paracetamol is filtered. The crude paracetamol is given charcoal treatment and pure paracetamol is recrystallized in water. The wet cake of paracetamol is centrifuged, dried and packed. The temperature control during acetylation may ensure complete acetylation of p-aminophenol and reduction of side products formation. The filtrate, after filtration of crude paracetamol, is dilute acetic acid solution containing unreacted p-aminophenol and paracetamol. Secondary acetylation may ensure that the conversion of p-aminophenol is complete. With solvent extraction, paracetamol could be recovered and dilute acetic acid could find some uses. The filtrate obtained after filtration of pure paracetamol could be re-used in the purification step 3-4 times before being discharged as effluent. Paracetamol could be recovered from this effluent by lowering its temperature or by solvent extraction or by salting out. This would improve the yields.

Experimental Work:

Considering the limited resources usually available to small and medium enterprises, it is apparent that only simple and low-cost wastewater treatment methods can be put into practice by these companies. Accordingly, work can be undertaken by using inexpensive adsorbents viz lignite, flyash, bentonite and activated carbon for studying adsorption characteristics with respect to the reduction of COD and color from concentrated wastewater streams from the pharmaceutical plant which contain phenolic compound.

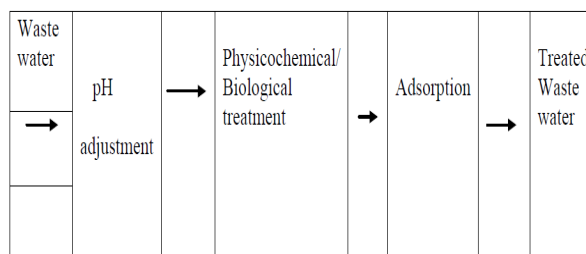
Adsorption of pollutants from effluent stream of paracetamol manufacture:

Objective:

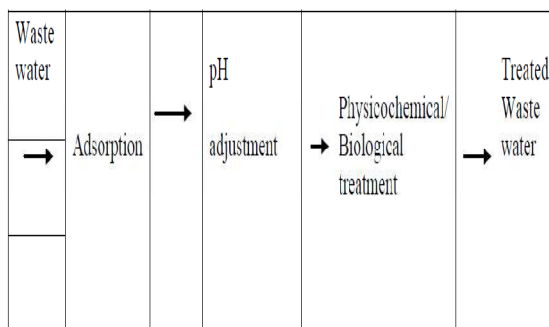
Whereas activated carbon is the most widely used adsorbent, it is found to be quite expensive. Considering the resource constraints experienced by the small scale industries, they use adsorption technique only if it is cost effective. Inexpensive adsorbents like lignite and bentonite could be, therefore, considered for detailed studies with respect to their performance in treating different waste water streams from paracetamol manufacturing plant.

Approach:

The conventional flow-sheets of industrial wastewater treatment shown below include the primary treatment oil and grease removal, pH adjustment and clarification, the secondary treatment which may consist of biological/chemical treatment and clarification, and depending on the quality of the waste water and the statutory discharge standards, tertiary treatment with activated carbon.



During primary treatment, neutralization of the waste water results in to increase of salts. Salts in high concentration inhibit biological activity and may cause an increase in non-settleable suspended solids in the treated waste water. The flow sheet shown below is, therefore, proposed wherein adsorption with inexpensive adsorbents is employed prior to the conventional primary treatment for increasing the efficiency of subsequent biological treatment.



This is expected to reduce refractory organics as well as BOD of the wastewater substantially at the first stage of wastewater treatment itself, facilitating further treatment.

Rathi-Puranik mathematical model:

Experimental data obtain in present investigation has been co-related by Rathi-Puranik equation which is as under:

$$\text{Log (CODRT)} = mt + C$$

Where,

$$\text{CODRT} = (c_i - c) / t$$

c_i = initial concentration

c = concentration at time t

T = time in minute

C = constant

Log (CODRT) values have been plotted against time in all the plots. Straight line nature of all the plots indicates that all the data obtained in the present investigation can be co-related satisfactorily by Rathi-Puranik equation.

Discussion for Pharmaceutical acidic effluent for COD values

Observation for COD value vs time for liquid effluent treatment using adsorbent activated carbon and lignite powder, this adsorption operation carried out in three stages.

Experiments and Results:

In this we do the experiments with Activated carbon and lignite. In which we take 250ml of effluent sample and we add activated carbon in terms of weight percent of effluent volume. similarly we do for the lignite and follow the standard method of GPCB for the COD testing. We take the readings for various time interval for activated carbon and lignite. We do Experiment with 1% to 4% activated carbon and lignite.

Experimental observation for COD reduction of acidic Pharmaceutical sample

Table -1 Adsorption with 1% activated carbon

Sample(250ml) with 1% activated carbon(2.5)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*10	%COD
initial	10	2.1	0.25	8000	10	1580	15800	-
10	10	2.25	0.25	8000	10	1550	15500	1.898
20	10	2.55	0.25	8000	10	1500	15000	5.063
30	10	2.9	0.25	8000	10	1420	14200	10.126
45	10	3.3	0.25	8000	10	1340	13400	15.189
60	10	3.75	0.25	8000	10	1250	12500	20.886
90	10.1	4.5	0.25	8000	10	1120	11200	29.114
120	10.1	5.05	0.25	8000	10	1010	10100	36.075

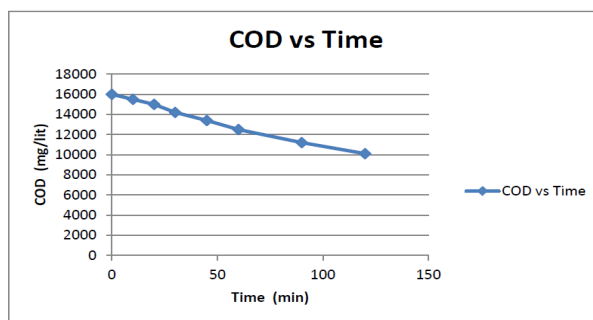


Fig: 2 Effect of Time on COD Reduction

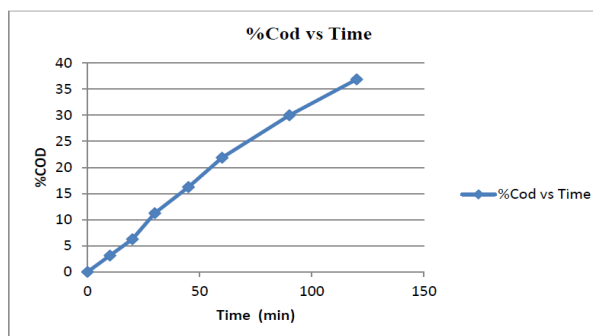


Fig : 3 %Cod Vs Time

Table: 2 Rate of Cod by Rathi-Puranik Model

ci	c	t mint	Codrt = (ci-c)/t	LOG(CODRT)
15800	15800	initial	-	-
15800	15500	10	30	1.477
15800	15000	20	40	1.602
15800	14200	30	53.33	1.726
15800	13400	45	53.33	1.726
15800	12500	60	55	1.740
15800	11200	90	51.11	1.708
15800	10100	120	47.5	1.677

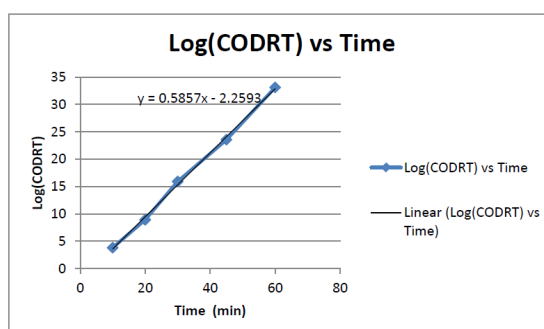


Fig: 4 Log(CODRT) Vs Time

Table-3 Adsorption with 2% activated carbon

Sample(250ml) with 2% activated carbon(5gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*10	%COD
initial	10.1	2.25	0.25	8000	10	1570	15700	-
10	10.1	2.55	0.25	8000	10	1510	15100	3.822
20	10.1	2.95	0.25	8000	10	1430	14300	8.917
30	10.1	3.5	0.25	8000	10	1320	13200	15.924
45	10.1	4.1	0.25	8000	10	1200	12000	23.567
60	10.1	4.8	0.25	8000	10	1050	10500	33.121
90	10.1	5.55	0.25	8000	10	912	9120	41.910
120	10.1	6.5	0.25	8000	10	720	7200	45.859

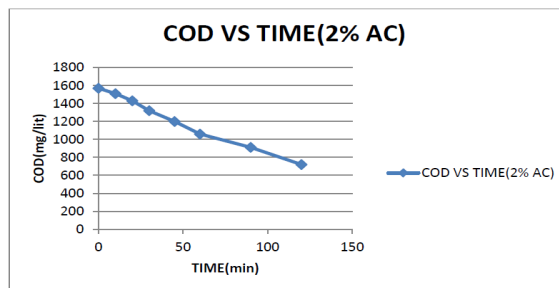


Fig: 5 Effect of Time on COD Reduction

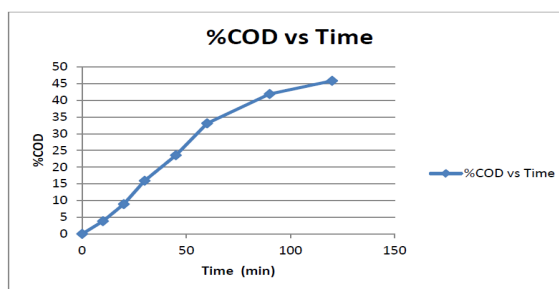


Fig: 6 %COD Vs Time

Table:4 Rate of COD by Rathi-Puranik Model

ci	c	t mint	Codrt =(ci-c)/t	LOG(CODRT)
1570	15700	initial	-	-
1570	15100	10	60	1.7781
1570	14300	20	70	1.845
1570	13200	30	83.33	1.9208
1570	12000	45	82.222	1.9144
1570	10600	60	85	1.9294
1570	9120	90	73.23	1.8653
1570	720	120	70.833	1.8502

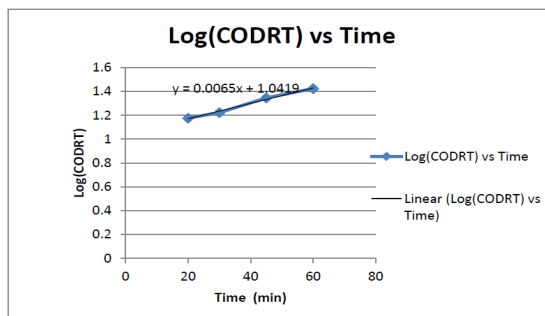


Fig : 7 Log(CODRT) Vs Time

Table: 5 Adsorption with 1% Lignite

Sample (250 ml) with 1% lignite (2.5gm)								
Time in min	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*10	%COD
initial	10.8	2.8	0.25	8000	10	1600	16000	-
20	10.8	2.95	0.25	8000	10	1570	15700	1.875
30	10.8	3.05	0.25	8000	10	1550	15500	3.125
45	10.8	3.3	0.25	8000	10	1500	15000	6.25
60	10.8	3.5	0.25	8000	10	1440	14400	8.75
90	10.8	3.7	0.25	8000	10	1420	14200	11.25
120	10.8	3.85	0.25	8000	10	1390	13900	13.125

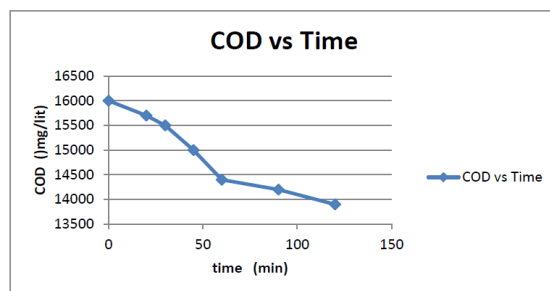


Fig: 8 Effect of Time on COD Reduction

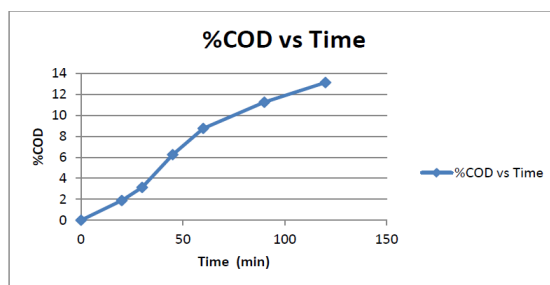


Fig : 9 %COD Vs Time

Table: 6 Rate of COD by Rath-Puranik Model

ci	T min	c	CODRT = (ci-c)/t	Log(CODRT)
16000	0	16000	-	0
16000	20	15700	15	1.176
16000	30	15500	16.67	1.222
16000	45	15000	22.22	1.346
16000	60	14600	13.33	1.124
16000	90	14200	20	1.301
16000	120	13900	17.5	1.243

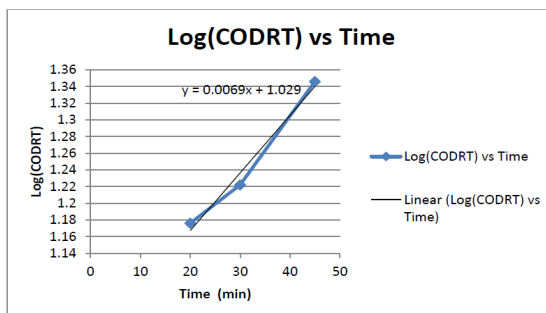


Fig: 10 Log(CODRT) Vs Time

Table: 7 Adsorption with 2% Lignite

Sample (250ml) with 2% lignite (5 gms)								
Time in min	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*10	%COD
Initial	10.9	2.9	0.25	8000	10	1600	16000	0
15	10.9	3.2	0.25	8900	10	1540	15400	3.75
30	10.9	3.4	0.25	8000	10	1530	15000	6.25
45	10.9	3.7	0.25	8000	10	1440	14400	10
60	10.9	4.05	0.25	8000	10	1370	13700	14.375
120	10.9	4.65	0.25	8000	10	1250	12500	21.875
150	10.9	5.4	0.25	8000	10	1110	11000	31.25
180	10.9	5.7	0.25	8000	10	1040	10400	35

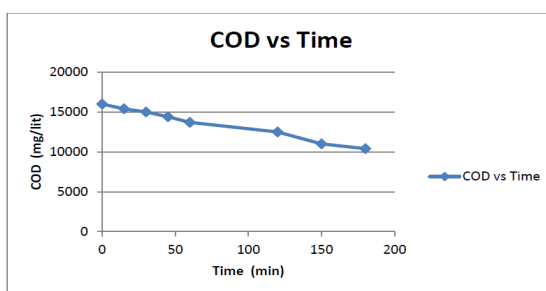


Fig: 11 Effect of Time on COD Reduction

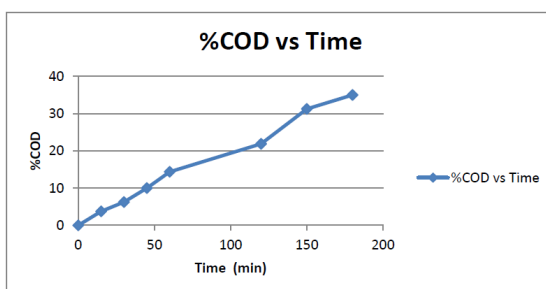


Fig: 12 %COD Vs Time

Table: 8 Rate of COD by Rathi-Puranik Model

ci	T min	c	CODRT=(ci-c)/t	LOG(CODRT)
16000	0	16000	0	0
16000	15	15400	40	1.602
16000	30	15000	26.67	1.425
16000	45	14400	40	1.602
16000	60	13700	46.67	1.669
16000	120	12500	20	1.301
16000	150	11000	50	1.698
16000	180	10400	20	1.301

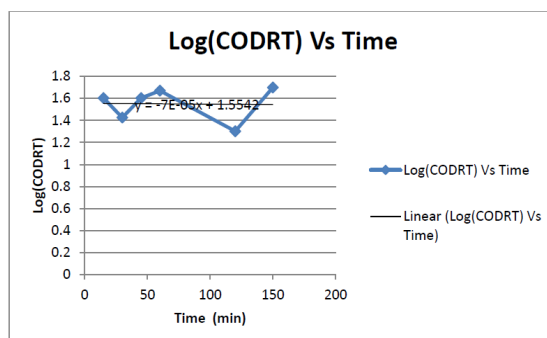


Fig: 13 Log(CODRT) Vs Time

Experimental observation for COD reduction of Neutralize Pharmaceutical sample

Table: 9 Adsorption with 1% Activated carbon

Sample(150ml) with 1% activated carbon(1.5gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*10	%COD
initial	10.2	5.15	0.25	8000	10	1010	10,100	-
10	10.2	5.35	0.25	8000	10	970	9700	3.96
20	10.2	5.6	0.25	8000	10	920	9200	8.91
30	10.2	5.9	0.25	8000	10	860	8600	14.85
45	10.2	6.3	0.25	8000	10	780	7800	22.77
60	10.2	6.8	0.25	8000	10	680	6800	32.67

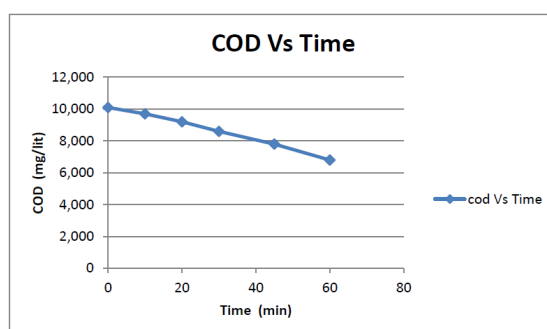


Fig: 14 Effect of Time on COD Reduction

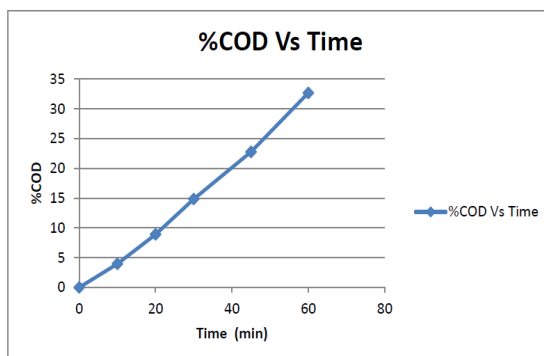


Fig: 15 %COD Vs Time

Table: 10 Rate of COD by Rathi-Puranik Model

ci	T min	c	CODRT = (ci-c)/t	Log(CODRT)
10100	0	10100	-	0
10100	10	9700	40	1.602
10100	20	9200	45	1.653
10100	30	8600	50	1.698
10100	45	7800	51.11	1.708
10100	60	6800	55	1.740

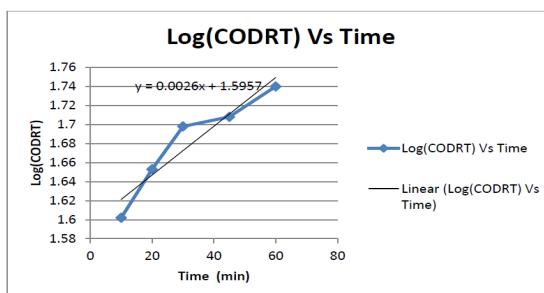


Fig: 16 Log(CODRT) Vs Time

Table: 11 Adsorption with 1% Lignite

Sample(150ml) with 1% Lignite(1.5gm)								
Time (min)	Blank reading	Sample reading	Normality of FAS	MW of oxygen	Volume of sample	COD	COD*10	%COD
initial	10.2	3.25	0.25	8000	10	1390	13900	-
10	10.2	3.4	0.25	8000	10	1360	13600	2.158
20	10.2	3.6	0.25	8000	10	1320	13200	5.035
30	10.2	3.85	0.25	8000	10	1270	12700	8.633
45	10.2	4.2	0.25	8000	10	1200	12000	13.67
60	10.2	4.75	0.25	8000	10	1090	10900	21.58

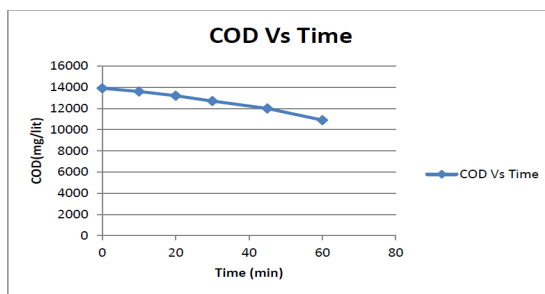


Fig: 17 Effect of Time on COD Reduction

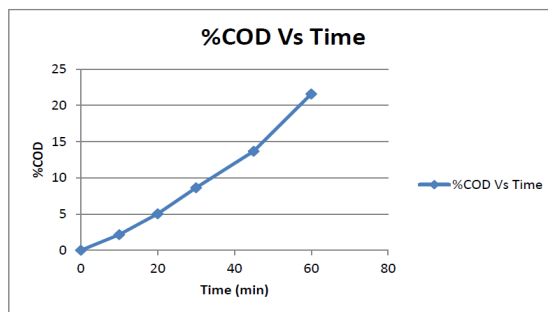


Fig: 18 %COD Vs Time

Table: 12 Rate of COD by Rathi-Puranik Model

ci	T min	c	CODRT = (ci-c)/t	Log(CODRT)
13900	0	13900	-	0
13900	10	13600	30	1.477
13900	20	13200	35	1.544
13900	30	12700	40	1.602
13900	45	12000	42.22	1.625
13900	60	10900	50	1.698

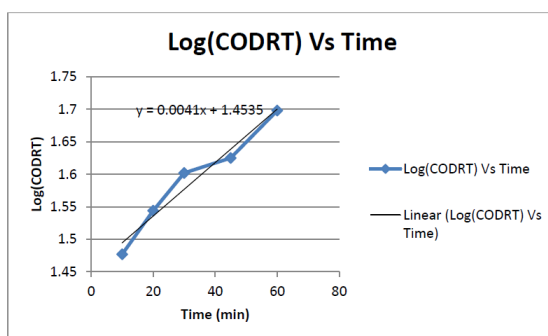


Fig: 19 Log(CODRT) Vs Time

Effect of time of contact:

As expected as time increase value of COD reduction increases with increase in time and after that stage reach when further increase in COD reduction value is practically increase small.

Thus it is seen from graph that as the contact of time increases from 10min to 2hr the reduction of COD value increases. Initially in the time period of 10min to 60min the span of COD reduction is higher than that of time period of 1hr to 2hr.

Further COD reduction values for the case of lignite powder are little lower than activated carbon under otherwise identical condition.

Effect of quantity of adsorbent:

Quantity of adsorbent is utilize has been change from 1% to 2% adsorbent used.

As expected when quantity of adsorbent is increases the values of COD reduction increases. Under the otherwise identical condition as quantity adsorbent increases from 1% adsorbent to 2% adsorbent COD reduction values increases substantially. However when quantity of adsorption increases from 3% to 4% the values of COD reduction increases marginally.

Comparision of adsorbent activated carbon and lignite powder

In the case of acidic effluent where in values of COD reduction were comparable slightly lower for adsorbent lignite powder than activated carbon.

In the second case where in neutral effluent has been consider for adsorption, similar trend is observed.

Hence activated carbon can be replaced by lignite powder since experimental result of COD reduction values do not differ much.

CONCLUSION

All the above observation for the two cases under consideration clearly indicate that values of CODRT for the case of acidic effluent are higher than the values of CODRT for the case of neutral effluent. Thus by modifying industrial effluent treatment flow sheet by carrying of adsorption operation initially than at the end, rates of CODRT can be increased under otherwise identical condition.

Hence, in industry, adsorption operation can be performed for contact time 30min and higher rates of COD reduction for acidic effluent can be utilized conveniently to carry out "Effluent Treatment" more effectively. Thus, either in existing plant, more quantity of effluent can be handled, or keeping effluent quantity same, effluent treatment can be carried for lesser contact time. Thus, operational cost can be decreased for the both categories.

REFERENCES

- [1] A. K. A Rathi & S. A. Puranik, *Chemical Engineering World*, Volume: XXIX, No: 10, October **1994**, pp: 45 – 51.
- [2] A. K. A Rathi & S. A. Puranik, *Research And Industry*, Volume: 39, September **1994**, pp: 143 – 146.
- [3] Dipak. S. Vyas, *Innovative treatment of Industrial waste: An Economically viable step towards environmental protection*; Birla Vishvakarma Mahavidhyalaya, Vallabhvidhyanagar; International Conference on Innovative Science & Engineering Technology – **2011** (8 – 9th April – 2011); V. V. P. Engineering College, Rajkot; Conference proceedings – ISBN: 978-81-906377-9-4, Page no: 70 – 73.
- [4] Guides to Pollution prevention in pharmaceutical industry Risk Reductio Engineering Laboratory and Center for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268
- [5] Daughton CG, Ternes TA. [**1999**] *Environmental Health Perspectives* 107: 907–942.
- [6] Satyawali Y., Balakrishnan M.(**2008**) Waste water treatment in Molasses-based alcohol distilleries for COD & color removal: A review *Journal of Environmental Management*,86,481-497. [This presents approaches to the study of Industrial waste water Treatment]
- [7] Chaudhari, R; Parande, M; Ramchandran, P. and Brahme, P. Iscre-8, Peragon Press, UK, 205, **1984**
- [8] *Journal of Hazardous Materials*, Performance evaluation of low cost adsorbents in reduction of COD in sugar industrial effluent Anand. K. Parande , A. Sivashanmugam, H. Beulah, N. Palaniswamy
- [9] Westerterp, K; van Gelder, k ;Janssen, H. and Oyevaar, M.*chem. Eng. Sci.*43, 229, **1988**
- [10] Fillion, B; Morsi, B; Heier, k. and Machado, *M. Ind. Eng. Chem. Res.*, 41, 697, **2002**
- [11] John MM, Marshall WE, Toles CA (1998). *J. Chem. Technol. Biotechnol.* 71: 131-140.
- [12]<http://www.gcpcgujarat.org/index.php?file=pha-rmaceutical>
- [13] www.cleanerproduction.com
- [14]www.c4cs.curtin.edu.au/resources/publications/2000/cp-processind.pdf
- [15] www.epa.sa.gov.au/pdfs/cpsmiths.pdf
- [16] www.uscentrifuge.com/potato-waste-solutions.htm - 31k
- [17] www.oceta.on.ca/documents/Humpty_fnl.pdf