Impact Factor (SJIF): 5.301

International Journal of Advance Research in Engineering, Science & Technology

e-ISSN: 2393-9877, p-ISSN: 2394-2444

Volume 5, Issue 5, May-2018

WASTEWATER (DYE INTERMEDIATE INDUSTRIES) TREATMENT BY CATALYTIC ADSORPTION (METALLIC-CATALYST)

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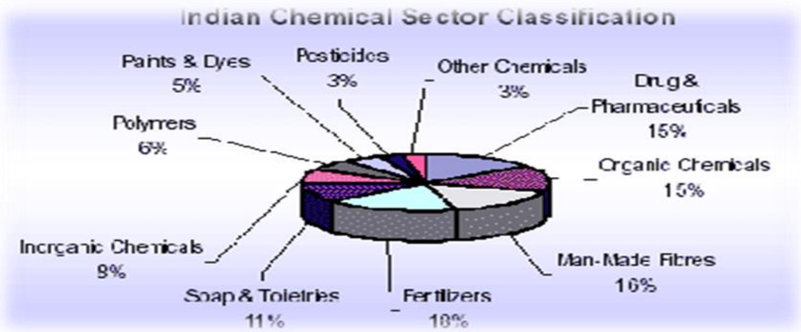
Introduction

Dye industry is an integral component of the Indian economy, which contributes around 7 % of the Indian GDP. It touches our lives in several different ways. Whether it is thermoplastic furniture we use, or a synthetic garment we wear, or a drug we take – we are inextricably associated to it. The industry is integral to the development of agricultural and industrial development in India and has key linkages with various other downstream, such as automotive, consumer durables, engineering, food processing and more.

Growing at an average rate of 12.5%, the Indian chemical industry offers a wide spectrum of opportunities for the investors both from India and the world. The significant market potential, coupled with the existing pool of human resources, and the comprehensive variety of resources in the country make it s profitable destination in the new millennium. In the world production of chemicals, Indian industry stands at 12th position.



Environmental impacts of Dyes intermediate and Dyes effluent:-

These chemicals persist in the environment, enter the food chain, bioaccumulate, biomagnify, and cause harmful effects in wildlife and humans. Because of aquatic contamination by these chemicals, bacteria and other microbes in the aquatic environment can become more resistant to these chemicals. This results in the development of more antibiotic resistant and virulent pathogens in the environment. Therefore, the persistence of pharmaceutical chemicals in the environment has become a global problem. **(Jones O.A et al, 2005b)**

Table- 1.1 General characteristics of dyes intermediate waste water:-

Sr. no	Parameter	Value
1	pH	4-6
2	Colour	Varying deep colour
3	COD	50000 – 100000 mg/l
4	TDS	15000 – 200000 mg/l
5	Sulphate	61000 to 73000 mg/l
6	Sodium	40000 to 47000 mg/l
7	chloride	16000 to 20000 mg/l

2 material & method

Experimental setup for Catalytic wet Air oxidation Process:

Catalytic Adsorption experiments were conducted in a glass reactor with having size 50cm (height) and diameter of 6.5cm. The Catalytic bed provided with 25cm height. 30% catalyst was mixed properly with activated carbon for catalytic adsorption. One water inlet provided at the bottom of the rector and one water outlet provided for the treated water collection. The top of the rector is kept open.

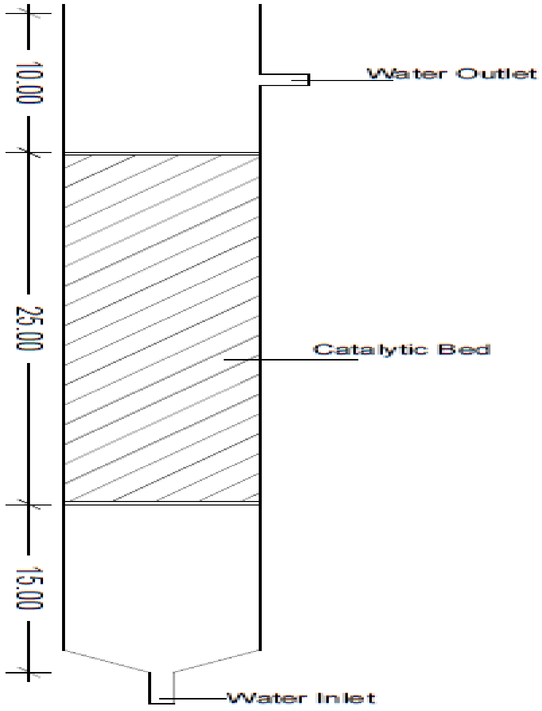


Figure 2.1 Experimental setup for Catalytic Adsorption process

Experimental procedure for Catalytic adsorption:-

1. Catalytic Adsorption experiments were conducted in a glass reactor.
2. The reactor was equipped with a perforated plate below and above catalytic bed.
3. For a typical duration run, the wastewater was supplied to reactor and the
predetermined amount of the catalyst with activated carbon.
4. Some aggregate were kept on upper perforatef plate so that plate do not float by effluent.
5. waste water is filled in bucket provided the tap and bucket is connected to reactor by pipe.
6. Reactor is kept on ground bucket is kept at some height to send effluent with force in reactor as shown in figure.
7. The effluent passes through activated carbon having catalyst in it and is collected from outlet of reactor.

Preparation of Activated Carbon:-

Green Coconut Shells were collected from nearby market and then cut into small pieces, followed by washing with simple tap water for removal of dust adhere to it. Then it was dried in the sunlight for 15-20 days. Dried materials were kept inside the furnace at 150°C for 24 hours for removal of moisture and other volatile impurities. After that it was crushed with a locally made crusher and sieved to 300-700 µm size range. Chemical Activation of the powdered precursor was done with $ZnCl_2$ to make the Impregnation Ratio (Activating agent/Precursor) 100% (500 gm of dried precursor was well mixed with 3000 ml of concentrated solution of $ZnCl_2$ that contains 500 gm of $ZnCl_2$). The slurry form of powder precursor was properly mixed and kept for 24 hours for proper soaking of $ZnCl_2$ on its surface. The slurry was kept inside the oven at 100°C for 24 hours. In this work we have used $ZnCl_2$ because it acts as dehydration reagent that lowers the carbonization temperature during chemical activation and restricts the formation of tar as well as promotes charring of carbon.

The resulting chemical impregnated samples were kept inside the muffle furnace after putting inside galvanized iron pipe of dimensions (ID 3.7 cm, OD 4.4 cm, Length 24 cm). The material inside the furnace was heated at a heating rate of 10°C min^{-1} to the final carbonization temperature. The material was kept inside the furnace for 1 hr at 650°C. The dried material was washed with 0.5 N HCl for 2-3 times and then washed with warm distilled water to remove different residual organic and mineral matter. Then it was finally washed with cold water till the solution becomes neutral. Finally the sample was dried for 24 hours at 100°C inside an oven and packed in an air tight container.[18]

8 Preparing Activated Catalyst :-

1) ZnO (Zinc Oxide)

2) TiO_2 (Titanium dioxide)

3) Fe_2O_3 (Ferric oxide)

Catalyst were activated by mixing 35% concentrated HCL in catalyst. HCL was added to make catalyst slarry and then it was mixed well. After that catalyst was kept for drying at room temperature till it was completely dry.

Adsorption isotherms

The free gas and the adsorbed gas are in dynamic equilibrium, and the fractional coverage of the surface depends on the pressure, P, of the overlying gas. The variation of θ with pressure at a chosen temperature is called the adsorption isotherm.[19]

The Langmuir isotherm

This simplest physically plausible isotherm is based on three assumptions:

1. Adsorption cannot proceed beyond monolayer coverage.
2. All surface sites are equivalent and can accommodate, at most, one adsorbed atom.
3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites and there are no interactions between adsorbed molecules.

The dynamic equilibrium is:

$$A(gas) + M(surface) \Leftrightarrow AM(surface) \qquad (1)$$

With rate constants k_a for adsorption and k_d for desorption. At equilibrium the rate of change of θ due to adsorption should be equal to the rate of change of θ due to desorption, so there is no net change of fractional coverage θ. The dependence of θ on pressure is called the Langmuir isotherm:

$$\theta = \frac{n}{n_s} = \frac{Kp}{1+Kp} \qquad K = \frac{k_a}{k_d} \qquad (2)$$

Where n is the number of adsorbed molecules (mol); n_S is the number of surface sites (or, in other words, the number of molecules required to create a monolayer) (mol); K is the adsorption rate (Torr^{-1}). By measuring P and n the number of surface site and the adsorption rate can be calculated:

$$\frac{P}{n} = \frac{P}{n_s} + \frac{1}{Kn_s} \qquad (3)$$

A plot of P/n against P would be a straight line with a slope of $1/n_S$ and intercept at $1/Kn_S$.

When the adsorption is accompanied by dissociation, the Langmuir isotherm becomes more weakly dependent on pressure:

$$\theta = \frac{\sqrt{KP}}{1+\sqrt{KP}} \qquad (4)$$

The shape of the Langmuir isotherm is shown in Figure . As can be seen, θ increases with pressure, until gas is forced on to every available site of the surface and $\theta \rightarrow 1$.

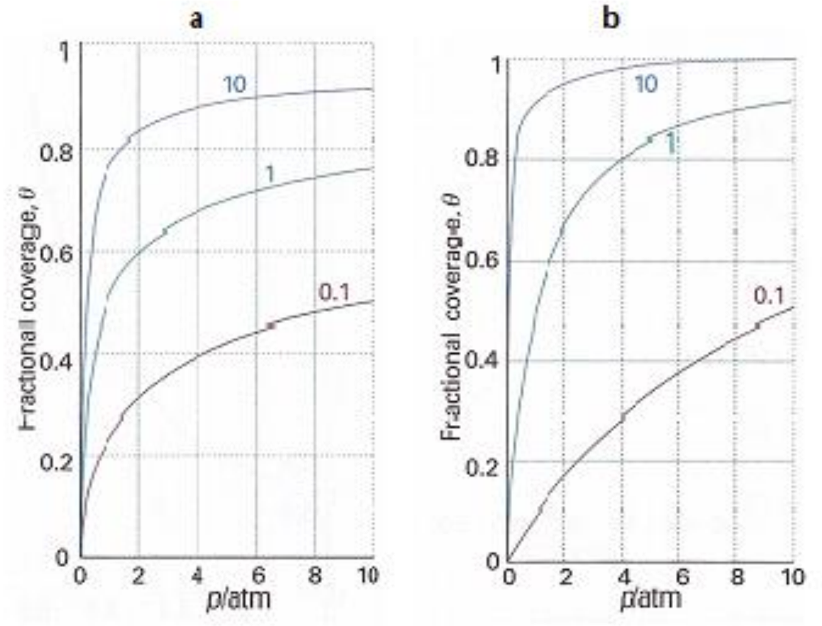


Figure 2.2 The Langmuir isotherm for different values of *K*: (a) non-dissociative adsorption; (b) dissociative adsorption, X_2(gas) → 2X(surface)[19]

3 RESULT& DISCUSSION

Adsorption using Activated Carbon in reactor for batch process

- COD OF EFFLUENT = 3570
- BATCH PROCESS:-
- BLANK READING = 22.8 ml

Table – 3.1 COD reduction by Activated Carbon.

SR. NO.	MATERIAL USED	SAMPLE	BURETTE READING	COD	Reduction
1	ACTIVATED CARBON	2 ml	20.72	822.85	76.95
2		2 ml	20.80	791.20	77.84
3		2 ml	20.64	755.60	78.83

Catalytic Adsorption using ZnO as catalyst in reactor for batch process

- COD OF EFFLUENT = 3570
- BATCH PROCESS:-
- BLANK READING = 22.8 ml

Table – 3.2 COD reduction by ZnO as catalyst with AC.

SR. NO.	CATALYST USED	SAMPLE	BURETTE READING	COD	Reduction
1	ZnO	2 ml	20.98	719.99	79.83
2		2 ml	20.88	759.55	78.72
3		2 ml	20.85	771.42	78.39

3 Catalytic Adsorption using TiO_2 as catalyst in reactor for batch process

- COD OF EFFLUENT = 3570
- BATCH PROCESS:-
- BLANK READING = 22.8 ml

Table – 3.3 COD reduction by TiO_2 as catalyst with AC.

SR. NO.	CATALYST USED	SAMPLE	BURETTE READING	COD	Reduction
1	ZnO	2 ml	21.99	320.44	91.02
2		2 ml	21.96	332.30	90.69
3		2 ml	21.91	352.08	90.14

Catalytic Adsorption using Fe_2O_3 as catalyst in reactor for batch process

- COD OF EFFLUENT = 3570
- BATCH PROCESS:-
- BLANK READING = 22.8 ml

Table – 3.4 COD reduction by Fe_2O_3 as catalyst with AC.

SR. NO.	CATALYST USED	SAMPLE	BURETTE READING	COD	Reduction
1	ZnO	2 ml	21.48	522.19	85.37
2		2 ml	21.43	541.97	84.82
3		2 ml	21.38	561.75	84.26

Catalytic Adsorption using different catalyst in continuous process -1

- COD OF EFFLUENT = 3570
- CONTINUOUS PROCESS:-
- BLANK READING(B) = 22.8 ml

Table – 3.5 COD reduction by ZnO as catalyst with AC.

SR. NO.	CATALYST USED	SAMPLE	BURETTE READING	COD	Reduction
1	ZnO	2 ml	20.36	965.26	72.96
2		2 ml	20.29	992.95	72.18
3		2 ml	20.47	921.75	74.18

Table – 3.6 COD reduction by TiO_2 as catalyst with AC.

SR. NO.	CATALYST USED	SAMPLE	BURETTE READING	COD	Reduction
1	TiO_2	2 ml	21.45	534.06	85.04
2		2 ml	21.39	557.80	84.37
3		2 ml	21.36	569.66	84.04

Table – 3.7 COD reduction by Fe_2O_3 as catalyst with AC.

SR. NO.	CATALYST USED	SAMPLE	BURETTE READING	COD	Reduction
1	Fe_2O_3	2 ml	20.81	787.24	77.95
2		2 ml	20.77	803.07	77.50
3		2 ml	20.86	767.46	78.50

Catalytic Adsorption using Activated Carbon in continuous process.

- COD OF EFFLUENT = 3650
- CONTINUOUS PROCESS:-
- BLANK READING = 24.65 ml

Table – 3.8 COD reduction by AC.

SR. NO.	MATERIAL USED	BURETTE READING	COD	Reduction	Volume passed(litres)	Time
1	ACTIVATED CARBON	22.55	830.76	77.23	1.8	1 hour
2		22.37	901.97	75.31	3.37	3 hour
3		22.19	973.18	73.34	4.62	6 hour
4		21.89	1091.86	70.14	2.68	8 hour
		21.67	1178.89	67.64	1.18	9 hour

Conclusion and future scope:-

The study culminates in the development of a hybrid process in abatement of one environmental problem of the industries. The removal of COD from Intermediate Dye Industry wastewater was conducted successfully on a laboratory scale. The Scope of this research or experiment was to study the Catalytic adsorption process by the use of different catalysts for the treatment of Intermediate dye industry wastewater. After treatments using different catalysts given to the wastewater, following conclusion should be drawn in respect of the COD reduction of wastewater.

Catalytic Adsorption using Activated carbon and ZnO, TiO_2, Fe_2O_3 as catalyst in batch process:

- By using AC (Activated carbon) and ZnO as catalyst COD of the wastewater effluent was reduced up to 70%.
- By using AC (Activated carbon) and TiO_2 as catalyst COD of the wastewater effluent was reduced up to 82%.
- By using AC (Activated carbon) and Fe_2O_3 as catalyst COD of the wastewater effluent was reduced up to 75%.
- Color change in wastewater was observed after Treatment in all catalyst which were used and effluent water which was in brownish colour became nearly colourless.

Catalytic Adsorption using Activated carbon and ZnO as catalyst in continuous process in reactor:-

- By using AC (Activated carbon) and ZnO as catalyst COD of the wastewater effluent was reduced up to 90%.
- Color change in wastewater was observed after Treatment.

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