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Adsorption of Dyes through Clay Adsorbent

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Abstract— The aim of this research paper is to investigate and identify the use of clay adsorbent in order to treat waste water from textile industries, and to make recommendations for industries where wet processing is carried out for Dyeing fabrics. Although a lot of waste water treatments are incorporated, but at present a cost effective and operationally feasible method is required. This identifies the uses of clay adsorbents for removal of two reactive dyes Procion Red HEXL & Procion Yellow HEXL of Dystar Japan. The paper comprised of useful practical work on the physiochemical process, including uses of centrifuge and digital spectrometer for studying changes after deployment of clay adsorbents in the stalk solution of Dyes. The paper throws light on the adsorption capacity and removal ratio of Cationic, Anionic and Neutral adsorbent. Kaolin showed higher adsorption capacity under acidic condition than neutral and alkaline condition. At present studies carried out using Kaolin as effective adsorbent for removal of dyes. The removal efficiency of Kaolin relatively stable above 50% until the initial dye concentration reached at 160 $mg.L^{-1}$ of both reactive Procion dyes when the liquid/solid ratio of 50 $mL.g^{-1}$ and this paper after thorough research & experimentation concludes, Charcoal is even better adsorbent with respect to removal ratio efficiency as its above 80% when initial concentration reached 160mgL^{-1}, it's also economically feasible. This research paper hopes to make small contribution to improving the waste water treatment obtained as a result of Dyeing and its utilization in other operations.

Index Terms — Wet Process, Dyeing, Adsorption, Physiochemical process, Spectrometer, adsorption Capacity, Removal paper.

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1 Introduction

The disposal of waste water from Dyeing units has been a problem for many decades because the Dyestuff does not degrade easily. Where a large amount of water in dumps and landfills causes pollution and environmental hazard, it also provides a toxic threat for aquatic life. This is not the only impact the presence of Phenolic, carboxylic, aromatics, metallic & phosphoric groups also lead to serious ailments like cancer, hepatitis, skin irritation and loss of vision in human societies near such dyeing units. These are some major problems caused by waste water. The renowned biochemical treatment does have good results against COD, BOD of such upstream but the degradation of dyestuff molecules is even complex for enzymes. Environmentally safe and feasible new recycling technologies can prove to be helpful in this regard. A better solution from an economic and environmental standpoint is to introduce clay adsorbents to reprocess the water and its utilization in any further operation like heat exchange or utilities. A very small amount of adsorbent in comparison of initial concentration of dyes is consumed. So the process is cheap too.

2 History

The manufacture of Synthetic dyes dates back to1800s. There feasibility for long term use is enhanced by their optimization so that they can withstand physical and chemical agents without fading. These improved properties fabrics durability has majorly increases and the textile industry has flourished. However, a great amount of the synthetic dyes used in the dyeing of fabrics goes in water. To eliminate these molecules is very difficult, which represent a danger for the environment and for the masses working in textile these days. In fact, in number of the textile producing countries, dyes from effluents are adsorbed to available materials or precipitated so that the water becomes clear, but huge quantity of toxic sludge are accumulated and consumed, for example, to build roads. In previous years the legislation has introduced stricter parameters to meet the elevating concern for the conditions of the workers and the eco system. Thus, more efficient strategies to treat the water from dyes need to be formulated so that no toxic by-products are generated.

3 Environmental Implications

The objective of this research is to evaluate different physical adsorption processes for their ability to degrade dyes to non-toxic chemical species and use the conclusion to expedite a novel approach for treatment of textile wastewater which can available higher efficiency in terms of water purification at feasible cost and environmental influence. In fact Textile industry is in magnificently requires to lessen its negativity on the environment and to be more “Green”. To pursue treatment of textile wastewater is one of the ways in this objective. The objective of this research is to evaluate different physical adsorption Processes for their ability to degrade dyes to non-toxic chemical species and use the conclusion to expedite a novel approach for treatment of textile wastewater which can available higher efficiency in terms of water purification at feasible cost and environmental influence. In fact Textile industry is in magnificently requires to lessen its negativity on the environment and to be more “Green”. To pursue treatment of textile wastewater is one of the ways in this objective. The textile industry is one of the biggest and most historical on the planet. The textiles production, once existed all over the world, has locomoted to countries where the costs of raw materials and labor are cheap. More than HALF of the total textiles of the USA and EU are imported from Asia, certainly China, Pakistan, India & Bangladesh. In these countries the textile industry has become one of the major business sectors, and eminent struggle is continuously made to propagate production. The textile industry consumes great quantity of water. The research project focuses on removal of dyes from the huge quantity of water to be re- use of the upstream water in the process. This will not only forbid wastage of water but will open new doors for recycling it in the different operations like utilities, cooling towers, floor cleaning etc. . We must incorporate changes in the chemical processes in order to eradicate harm for natural eco system. This is to save our water resources.

4 Textile Process

The Textile Process has following steps to go through before getting a useful product.

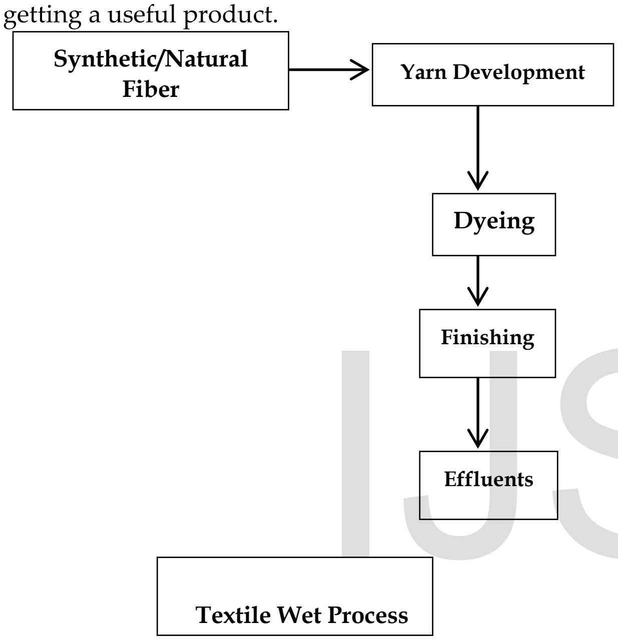

Figure 1 Main steps of a typical textile production generation of wastewater during the wet processing.

4.1 Textile Waste Water

Enormous amount of premium-quality water are required for wet processing of fabrics. The theoretical consumption goes from 50-240 liters of aqua per kilogram of finished textile relevant upon the shade, technicality and the chemicals used in a specific textile Process.

4.2 Components oF Textile Waste Water

The wastewater contents can vary, but the peculiar characteristics are: high organic content;

- Dyestuff
- inorganic compounds like Sodium Carbonate,
- Buffers;
- Salts
- Caustic Soda
- Softening Agents
- Detergents

In addition, pH of textile effluents is in range of 4-12 often having high temperature. The effluent often contains Insoluble fibers that may cause clogging of pipes. The wastewater streams generated in different steps of the textile process coincide to form the so-called textile wastewater. The effluent created during the manufacturing steps usually consists of

- Cleansing agents (Syndents) used to clean wax and other impurities from the fabrics
- Enzymes for neutralizing the sizing agents
- Sizing agents such as starch, polyvinyl alcohol (PVA), carboxyl methyl cellulose (CMC) and poly acrylic acid and
- Bleaching agents

4.3 Removal of Impurities

Thus, the above study on waste water of textile industry concludes that the effluent stream consist of different types of impurities which are removed by employing specific biological and chemical techniques in order to carry out a sustainable process.

5 Dyes Degradation Evaluation Techniques

5.1 UV-visible absorbance

The simplest but reliant technique to access the dyes degradation is based on their ability to absorb light. This is useful in evaluating the quality of a textile effluent and performance of a treatment process. Light absorbed in dyes is in visible range, but upon degradation they lose this ability. In particular dyes undergo cleavage of the bond easily which results in the aromatic amines formation and disappearance of color at the same time. The amines are toxic and mutagenic although colorless and to degrade them further is necessary, into inorganic compounds possibly. Thanks to the aromatic structures most dyes and also the aromatic amines produced as a result of decolonization can also absorb light in the UV range.
Thus, the degradation of these structures by measuring the UV absorbance can be followed. Every dye has its own specific absorbance spectrum, a property that is very utilizable for model systems where only one dye molecule is involved.

6 Experimental Techniques for Dyestuff Removal

6.1 Material Preperation

The Dyestuff Procion Red H-EXL & Procion Yellow H-EXL obtained from Dystar Japan. Clay adsorbents like KAOLIN, BENTONITE & CHARCOAL were taken from local firms.

6.2Adsorption Methodology

Adsorption Methodology First of all stalk solutions of both dyes was prepared in ppm from 40-200 mg/L each in distilled water. The magnetic stirrer used for uniform mixing. The absorbance of all these concentrations were recorded and observed by using Digital Spectrometer. The actual wavelength λmax of Procion Red HEXLis 535nm & 418nm in case of Procion Yellow HEXL which are already fed to the spectrometer. The specified amount i.e. 1 gm. each of clay adsorbents were added in 50 ml of each concentration. The sample was then kept for contact time of almost 16-18 hours at room temperature. The 20ml of each of the sample was then taken in the test tube for centrifuge at 2000RPM. This helps in the gravitational settling of all the solute at the bottom. This sample is again filtered using WATTMAN's filter PAPER NO 1 in order to clear the filtrate from any residual traces of dye and adsorbent. The 6 ml of this filtrate of each concentration is taken into spectrometer where the absorbance is again observed. The initial concentration, initial absorbance & final absorbance were used to calculate the final concentration. Thus, the final concentration calculated is then used to reveal below parameters:

- **Adsorption Capacity &**
- **Removal Ratio**

7 Calculations for Final Absorbance

After adsorption the final Concentration is unknown for both Dyes and is calculated through TREND feature in MS Excel.

7.1 Calculations of Procion Red H-EXL

Table 1 Final Absorbance of Procion Red H-EXL with Bentonite

Initial Concentration ppm	Initial Absorbance (AU)	Final Concentration ppm	Final Absorbance (AU)
40	0.84	16.21	0.59
80	1.67	34.52	0.88
120	2.51	58.36	1.25
160	3.02	76.94	1.54
200	3.02	99.47	1.89

Table 2 Final Absorbance of Procion Red H-EXL with Kaolin

Initial Concentration ppm	Initial Absorbance (AU)	Final Concentration ppm	Final Absorbance (AU)
40	0.84	30.86	0.82
80	1.67	62.21	1.32
120	2.51	99.31	1.92
160	3.02	136.0	2.49
200	3.21	171.0	3.06

Table 3 Final Absorbance of Procion Red H-EXL with Charcoal

Initial Concentration ppm	Initial Absorbance (AU)	Final Concentra-tion ppm	Final Absorbance (AU)
40	0.84	3.06	0.38
80	1.67	11.19	0.15
120	2.51	13.00	0.12
160	3.01	30.00	0.81
200	3.20	75.14	1.53

7.2 Trend of Procion Red HEXL

The final concentration decreases in case of all three adsorbent. The final absorbance also proves the results as values for absorbance also decreases which show that dye is removed substantially. It shows that dye removal is fair for Bentonite better for Kaolin and exceptionally good in case of Charcoal.

7.3 Calculations of Procion Yellow H-EXL

Table 4 Final Absorbance of Procion Yellow H-EXL with Bentonite

Initial Concentration ppm	Initial Absorbance (AU)	Final Concentra-tion ppm	Final Absorbance (AU)
40	0.58	6.84	0.21
80	1.07	50.86	0.73
120	1.59	77.00	1.04
160	2.02	104.0	1.36
200	2.47	140.0	1.78

Table 5 Final Absorbance of Procion Yellow H-EXL with Kaolin

Initial Concentration ppm	Initial Absorbance (AU)	Final Concen-tration ppm	Final Absorbance (AU)
40	0.58	6.7	0.044
80	1.07	20.35	0.37
120	1.59	35.02	0.54
160	2.03	55.79	0.79
200	2.47	97.59	1.28

Table 6 Final Absorbance of Procion Yellow H-EXL with Charcoal

Initial Concentration ppm	Initial Absorbance (AU)	Final Concentration ppm	Final Absorbance (AU)
40	0.58	0.20	0.06
80	1.07	4.20	0.11
120	1.59	8.14	0.16
160	2.33	26.91	0.40
200	2.47	41.39	0.59

7.4 Trend of Procion Yellow H-EXL

The final concentration decreases in case of all three adsorbent. The final absorbance also proves the results as values for absorbance also decrease shows that dye is removed substantially. It shows that dye removal is fair for Bentonite, better for Kaolin and exceptionally good in case of Charcoal.

8 Adsorption Capacity

The adsorption Capacity is defined as the ratio of adsorbate to the unit mass of adsorbent. It is considered commonly as a parameter for determining the adsorbents potential. Higher the adsorption capacity with low equilibrium concentration of adsorbate the finer would be ability for the adsorbate separation adsorbate the finer would be ability for the adsorbate separation.

8.1 Calculations for Adsorption Capacity

The adsorption capacity is calculated by following formula:

$$Q_e = \frac{(C_i - C_f)\,V}{M}$$

Here, Q_e is adsorption Capacity,

C_i is initial Concentration in mgL^{-1},

C_f is final Concentration mgL^{-1},

V is volume of solution in L, and

M is mass of adsorbent.

8.2 Adsorption Capacity of Procion Red H-EXL

The graph between Final Concentrations and Adsorption Capacities of all the three clay adsorptions has same trend i.e. adsorption capacity is enhanced as the final concentration of Procion Red H-EXL increased. So this is evident from graphs showing straight line.

Table 7 Adsorption Capacity of Procion Red Hexl at different Concentrations

BENTONITE		Kaolin		Charcoal	
Final Conc. ppm	Adsorption Capacity	Final Conc. ppm	Adsorption Capacity	Final Conc. ppm	Adsorption Capacity
6.2	1.2	30.9	0.46	3.06	1.85
34.5	2.3	62.2	0.89	11.2	3.44
58.4	3.1	99.3	1.03	12.9	5.35
77.5	4.2	136	1.22	29.9	6.5
99.5	5.1	170	1.45	75.1	6.2

8.3 Adsorption Capacity Of Procion Yellow H-EXL

The graph between Final Concentrations and Adsorption Capacities of all the three clay adsorptions has same trend i.e. adsorption capacity is enhanced as the final concentration of the Dye Procion Yellow H-EXL increased.

Table 8 Adsorption Capacity of Procion Yellow Hexl at different Concentrations

BENTONITE		Kaolin		Charcoal	
Final Conc. ppm	Adsorption Capacity	Final Conc. ppm	Adsorption Capacity	Final Conc. ppm	Adsorption Capacity
6.8	1.66	6.7	2.3	5.6	2.28
50.9	1.45	20.3	2.9	1.3	4.06
76.9	2.15	35.02	4.25	3.05	5.84
103	2.80	55.8	5.2	23.53	6.82
139	3.03	97.6	5.1	39.32	8.03

9 Removal Ratio

The removal gives an account of percentage dye removal
It tells how much dye can be removed as the initial concentration increase. The formula used to calculate it as follows:

$$R = \frac{(C_i - C_f) \times 100}{C_i}$$

Where, C_i is the initial Concentration,

C_f is the final concentration or it is the residual concentration of dye left after adsorption. R is the removal ratio in percentage.

9.1 Calculations for Removal Ratio of Procion Red HEXL

Table 9 Removal ratio of Procion Red Hexl at different Concentrations

Initial Conc. ppm	REMOVAL RATIO Bentonite	REMOVAL RATIO Kaolin	REMOVAL RATIO of Charcoal
40	58.85	87.59	92.34
80	49.29	66.45	89.01
120	35.31	44.26	88.22
160	30.65	35.97	81.28
200	26.53	31.60	62.43

9.2 Explanation of Results of Procion Red Hexl

The Calculations regarding removal ratio of Procion Red Hexl show that with increased initial concentration the Removal ration decline linearly as the adsorbent mass is kept constant at 1 gram.This is true for all the three clay adsorbents but the removal ratio of Procion Red Hexl is amazingly greater with neutral adsorbent i.e. Charcoal. The removal ratio for is maximum at initial concentration of 40mg/L for the adsorbent. Contrary to 92% removal at this concentration the removal ratio is lagged 30% at 200 mg i.e. 62% the removal ratio is better in case of Kaolin but less than Charcoal it is 87%. It declines as the initial concentration increases and fall at 31% at 200mg/L. The removal ratio at initial concentration of 40mg/L in case of Bentonite is 58%. It decreases to 26% when initial concentration reaches 200mg/L.

9.3 Calculations for Removal Ratio of Procion Yellow HEXL

Table 10 Removal ratio of Procion Yellow Hexl at different Concentrations

Initial Conc. ppm	REMOVAL RATIO Bentonite	REMOVAL RATIO Kaolin	REMOVAL RATIO of Charcoal
40	82.89	94.17	99.51
80	36.42	74.55	94.75
120	35.91	70.81	93.21
160	35.02	65.13	83.17
200	30.37	51.20	79.30

9.4 Explanation of Results of Procion Yellow Hexl

The Calculations regarding removal ratio of Procion Yellow Hexl show that with increased initial concentration the Removal ration decline linearly as the adsorbent mass is kept constant at 1 gram. This is true for all the three clay adsorbents but the removal ratio of Procion Yellow Hexl is surprisingly greater then Procion Red HEXL as it wavelength is smaller in comparison to it With neutral adsorbent i.e. Charcoal. The removal ratio for is maximum at initial concentration of 40mg/L for the adsorbent. Contrary to 99% removal at this concentration the removal ratio is decrease only20% at 200 mg i.e. 72%. The removal ratio is better in case of Kaolin but less than Charcoal it is 94%. It declines as the initial concentration increases and fall at 51% at 200mg/L. The removal ratio at initial concentration of 40mg/L in case of Bentonite is 82%. It decreases to 30% when initial concentration reaches 200mg/L.

10 Effects of pH on Adsorption Capacity and Removal Ratio

The effect of pH on removal ratio of Dyes is checked against two adsorbent whose removal ratio at ambient conditions i.e. at neutral pH were maximum was observed by making pH lesser and higher with use of Hydrochloric Acid & Sodium Hydroxide.

10.1 Comparison of Removal Ratio of Procion Red H-EXL by varying pH

The removal Ratio of Procion Red Hexl is enhanced when ANIONIC ADSORBENT Kaolin is added in it with slight acidity. The removal at higher pH is not appreciable in the comparison with it. Similar trend observed in the removal ratio of Charcoal was different as initially removal ratio was same but gradually it was better with acidic environment. The trend shows that removal ratio is enhanced in acidic environment.

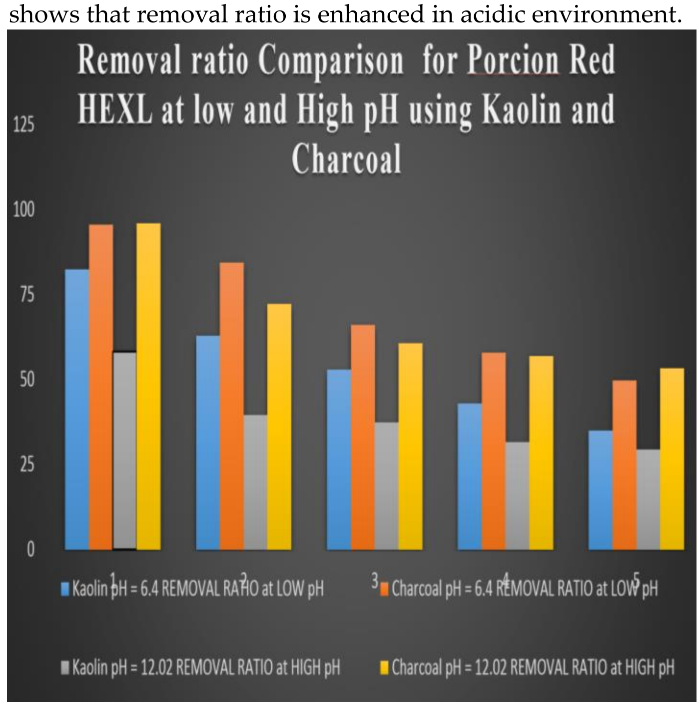

Figure 2: Removal Ratio of Procion Red Hexl at varied pH

10.2 Comparison of Removal Ratio Procion Yellow Hexl at different pH

The removal Ratio of Procion Yellow Hexl is also enhanced when ANIONIC ADSORBENT Kaolin is added in it with slight acidity like in Procion Red Hexl. Same trend for removal ratio is observed at higher pH. Similar trend observed in the removal ratio of Charcoal was different as initially removal ratio was same but gradually it was better with acidic environment. The trend shows that removal ratio is enhanced in acidic environment.

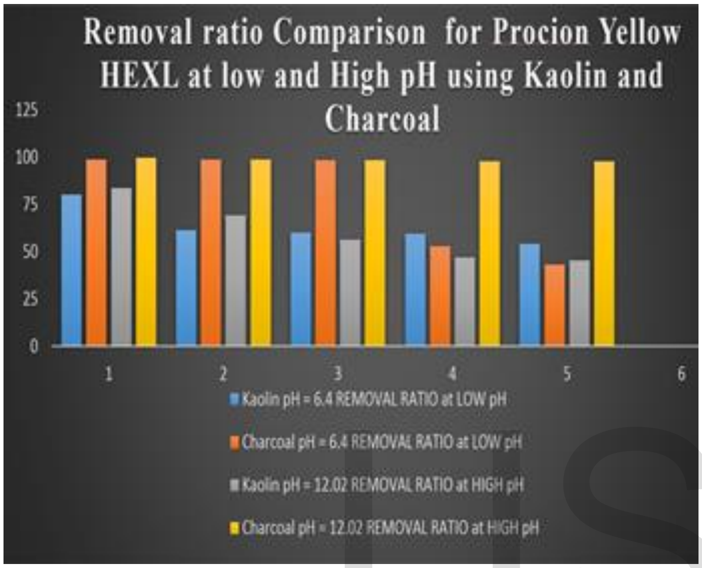

Figure 3: Removal Ratio of Procion Yellow Hexl at varied pH

11 Conclusions

From the above research we can infer that clay minerals Bentonite and Kaolin are good to use for dye removal but Activated Charcoal is an adsorbent which has the best removal percentage in comparison with the Cationic and Anionic Adsorbents. So, adsorption Technique can be employed for removal of Azo dyes by deploying Clay adsorbent. More over the dye removal is even more effective as pH drop.

12 Cost Effective

The activated Charcoal is cheap and low cost in comparison with other adsorbents and it is more readily available near all facilities its fine granulated form due to large surface area can be adhered by dyes easily. But Kaolin which is a clay mineral also has good results for removal of dyes and can be employed for good treatment of dyes waste water

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