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Int J Pharm Bio Sci 2013 Oct; 4(4): (B) 1091 - 1099

Research Article **Chemical Engineering**

International Journal of Pharma and Bio Sciences **ISSN 0975-6299**

COLOR REMOVAL FROM DYE EFFLUENT BY USING COAGULATION TECHNIQUE

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ABSTRACT

Dyes are coloring compounds being extensively used in almost all industries and the indiscriminate disposal of dye wastewater poses one of the major problems on the environment. This effluent containing a variety of contaminants viz. Nature of acidic, caustic, dissolved solids and toxic compounds like organic, inorganic or heavy metallic. The micro toxins are developed due to coloring agents by forming chelating under suitable chemical environment. The objective of the present work is to investigate the effectiveness of chemical treatment on removal of color of simulated acid dye solutions. Two dye stuffs one belongs to acid group and other vat dye were employed and batch tests were conducted with three coagulants (Alum, Ferric chloride & Aluminium chloride) to access feasibility and also to study the optimum coagulant dosage . The study clearly indicates that Napthal-I responds effectively to both Alum & $AlCl_3$. Napthal-II responds effectively to Alum. Vat dye is moderately responded to FeSO4.7H2O. The removal probably due to physicochemical mechanism of coagulation and flocculation and/or chelating complexation type reactions. A perusal of color removal data suggest that the color mechanism is predominately physicochemical coagulation especially at alkaline P^H ranges, presumable due to absorption on to hydroxide flocs, and color removal at lower P^H ranges may be either due to physicochemical coagulation or chelation complex formation reactions. The study clearly indicates that optimum P^H system conditions, there is significant reduction in the chemical dosage requirements and in some cases a further increase in color removal. From the above studies it may be concluded that some of the Acid & Vat dye stuffs are amenable for their color removal and shows positive response for treatment by chemical process using various coagulants.

KEY WORDS : Dye solution, Alum, Ferric chloride, coagulation.

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INTRODUCTION

The industrial activities generate a large number and variety of waste products, which are generally discharged either into water streams or onto land. The nature of industrial wastes depends upon the industrial processes in which they originate. The problem of adequate handling industrial wastewaters causes more complex and much more difficult than sewage, because industrial wastewaters are heavily laden with organic or inorganic or mineral matter or with corrosive, poisonous, inflammable or explosive substances. The objective of wastewater treatment and management has widely expanded from simple nuisance control to include public health, environmental, aesthetic and ecological considerations. The discharge of untreated and partially treated waste waters from industries such as textile, dyeing operations, pulp and paper production, tanneries, food processing, chemical production and mining, refining operation may contribute color to the receiving waters. The discharge of colored effluent into water bodies or onto land, though less toxic, on the premise that colors is an indicator of pollution. Recognition of color as a priority pollutant and promulgation of environmental regulations limiting effluent color levels have prompted several investigators to orient their research efforts towards color removal studies. Unfortunately, there are many variables to be considered for effective color removal and recognition of this fact is of primary importance for development of effective treatment technology. Pei Wen Wong.et.al. 2007 says that the chemical treatment has a great potential for dye color removal mechanism. Unfortunately little information is available concerning the influence of chemical characteristics/nature of dyestuffs on the color removal. In spite of several research efforts, the problem of selectivity/suitability of chemical treatment for a given dye waste still remains unresolved. It is evident that this issue cannot be solved in a hit and misfashion. A systematic approach to the problem is necessary. To this end, an attempt was made in the present study to investigate the response of number of Acid & Vat dyes belonging to various applications, classes and chemical families, through treatment with Alum, Ferric Chloride, and Aluminium Chloride with due reference to their chemical characteristics, nature and probe into the mechanistic aspect of color removal[1].

MATERIALS AND METHODS

To investigate the feasibility of direct dyes and vat dyes color removal by chemical treatment with Alum, $AlCl_3$ and $FeSO_4$ following materials and methods were used in the present study.

Materials

Glassware

All glassware used in the present study was Pyrex quality manufactured by Borosil Glass limited, Bombay and marketed under the brand name ‘corning’. The Glass were cleaned with nitric acid and rinsed with water before use. They were further acid washed and rinsed with water after use and stored for subsequent use in further experiments.

Water

Water used in all experiments was laboratory-distilled water, redistilled using a glass distillation still. The P^H of this water was in the range of 6.8 to 7.1 and the specific conductivity 2 to 5 μ seimen’s/cm.

Instruments

Instruments used for present work were Colorimeter & P^H system from systronic industries; Horizontal shaker (100 rpm) from Yorco instruments, York Scientific industries.

Dyes and Chemicals

List of two dyes along with some of their characteristic and chemical properties chosen for the present study are given previously. All the chemicals used for chemical treatment are of analytical grade and their characteristics as presented previously. Acetic acid and Sodium Hydroxide were used for adjusting the P^H values of dye test solution to assess the effect of color removal.

Estimation of Dye Color Concentration

Dye-Color concentration in the present work, analyzed using Colorimeter according to the procedure outlined in the standard methods for examination of water and waste 18th edition, prescribed by APHA, AWWA, and WPCF of the United States. A standard curve was prepared to each dye to facilitate rapid determination of dye concentration and was used throughout[2].

EXPERIMENTAL PROCEDURE

Apparatus

1. Photo electric colorimeter 2.Reagent bottles 3.Horizontal shaker 4.P^H meter
5.Conical flask

Dyes

1. Napthal-I 2.Napthal-II 3.Vat dye.

Coagulants

1. Alum 2.Ferrous sulfate 3.Ferric chloride 4.Barium chloride 5.Aluminum sulfate
2. Aluminum chloride 7.Sodium hypo chloride 8.Aluminum oxide.

Experimental procedure

Test dye solution of 100 mg/l was prepared from dye stock solution & this solution is taken in the reagent bottles, varying doses of designated chemicals were added to study feasibility of color removal by chemical treatment and the P^H of the test mixture was adjusted when required. A number of such reagent bottles containing the test mixture depending upon the requirement were employed. Then the reagent bottles' containing test mixture was placed in a horizontal shaker operating at 30 shakings per minute, to facilitate effective mixing and precipitates formation. Then the reagent bottles containing reaction mixture were kept under undisturbed for 2 hrs for settlement of precipitation formed. At the end of clarification period, samples were withdrawn and pippeting out 10 ml portion and analyzed for color removal, dye experiment by measuring absorbance by using the calibration curve, prepared[3]. Optimum system P^H was found by adding 75% of the optimum chemical dose and the test mixture was varied from 1.0 to 12.0 and the P^H value producing maximum color removal (optimum P^H) determined.

RESULTS AND DISCUSSION

The study was undertaken to seek information regarding removal of color from direct dye stuffs by chemical treatment with commonly used chemicals like Alum, Aluminium Chloride and $FeSO_4\ 7H_2O$. Most of the organic direct dyes in aqueous phase exhibit a tendency to associate and form dimers (double molecules) or polymers (higher molecular aggregates). This self-aggregation of direct dyes in aqueous solution is an universal reversible process, being promoted by an increase dye concentration, electrolyte concentration, higher P^H and a decrease in temperature. Such aggregate are micelles may be ionize and forms the positive and negative charges. The negative charge is localized most often on an ionized sulfonate group or oxide group. The colloidal property of direct dyes in aqueous solution and their role has been recognized. The organic direct dyes inaqueous phase exhibit marked concentration effects and this has been related to deviation from the Beer's law at higher concentration range and correlated to the formation of dimer and polymer colloidal aggregates in water[4]. It is also established that the dye anion aggregate usually contain absorbed gentians or undissociated grouping. Various mechanisms have been put forward to explain aggregation of in aqueous phase and the nature of forces that overcome the mutual columbic repulsion forces of similar ions to favor aggregation is not clear. It is very likely that Vander Waal forces, hydrogen bonding, and interaction of π-electrons or coupling of electronic oscillators and hydrophobic interactions may be responsible. In present study, deviation from the Beer's Law was observed for all the dyes. Several factors such

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as dye concentration or dissociation and at high temperatures, the effects of dye concentration are reversible.

Choice of coagulant

Response of selected dyes to chemical treatment with alum, $FeSO_4$ $7H_2O$, $AlCl_3$ were assessed using batch test procedure. The color removal with different coagulants are tabulated, in Table 1, Table 2 and Table 3. It may be observed that Napthal-I is amenable to chemical treatment with Alum, $AlCl_3$. Different chemical classes of acid dyes exhibited different degrees of color removal & color removal varied even in same chemical class.. These variations in color removal made generalization in terms of chemical class are difficult. Napthal-I dye is treated by using different coagulants of same weight. Napthal-I is amenable to chemical treatment with Alum & $AlCl_3$. But Napthal-II is checked by varying Alum so here carry out the tests with $AlCl_3$ see in Table - 4. Napthal-II dye is treated by using different coagulants of same weight. Napthal-II is amenable to chemical treatment with Alum. For results see the Table - 5. Vat dye is treated by using different coagulants of same weight. Vat dye is amenable to chemical treatment with $FeSO_4$.7 H_2O shown in Table - 6.

Effect of coagulant dosage on color removal

After attaining maximum color removal, removal either remained constant thereafter or increased or decreased marginally with chemical dose. These results may be interpreted as indicating that two or more distinct types of reactions/mechanisms, either individually or collectively was responsible in effecting color removal. The first among them is the conventional chemical coagulation mechanism involving adsorption or interaction between polymeric cationic metal hydroxyl species and ionogenic anionic dye aggregates resulting in charge neutralization. This facilitated Vander wall forces to cause aggregation leading to formation of settle able flocs. Alternatively, a chemical feaction/interaction between inorganic anionic dye aggregates and the polymeric metal hydroxy species occurred possibly resulting in the formation of insoluble Alum or Ferric salt or Aluminium Chloride salt of the dye by a salting our phenomenon[5]. Manivannan (1985) observed that two acid dyes, Co massive Navy blue and xylene Green responded partially to treatment with Alum, $FeCl_3$ and Ammonium Ferrous Sulfate but color removal was poor with magnesium sulfate. However, all the above investigators did not attempt to explain the reasons for non-removal of color even in the same chemical class. Karthikeyan (1990) after a detail study on color removal from forty three different textile dyes encompassing Acid, Basic, Direct, Disperse, Vat, Reactive, Sulfur and several chemical classes of azo, monoazo, diazo, triazo, polyazo, AQ, TPM, Sulfur, Nitro's, Xanthenes, etc.

Attributed the reasons for poor color removal due to the intrinsic structural arrangement of the dyes influencing metal-dye interactions leading to formation of metal-due interactions leading to formation of metal-dye chelates/complexes. For illustration the various chemical dosages of coagulants are varied and tabulated. Variation of color removal at optimum dosage for Napthal-II dye with varying dosage of Alum is given in Table-7 . Graph-1 shows the maximum 78.39% color removal occurs at chemical dosage of 21 mg/100ml. Variation of color removal at optimum dosage for Napthal-I dye with varying $AlCl_3$ is given in Table- 8 and Graph-2. The maximum 99.83% color removal occurs at chemical dosage of 2 mg/100ml. Variation of color removal at optimum dosage for Vat dye with varying dosage of $FeSO_4.7H_2O$ is given in.Table -9 and Graph-3.The maximum 98.75% color removal occurs at chemical dosage of 6 mg/100ml.

Response of chemical dose at optimum P^H conditions

Because of the chemical and engineering significance, hydrogen effectiveness of the color removal by chemical treatment processes. Batch experiments were conducted at a system P^H of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 9.0, 10.0, 11.0 and 12.0.As outlined earlier removal of color might probably due to physicochemical mechanism of coagulation and flocculation and/or chelation complexation type reactions. A perusal of color removal data suggest that the color removal mechanism is predominately physicochemical coagulation especially at alkaline P^H ranges presumably due to adsorption on to hydroxide flocs and at color removal at lower P^H ranges may be either due to physicochemical coagulation or mainly due to chelation complex formation reactions. In general, there will be an appreciable reduction in chemical dose requirements at optimum system conditions like P^H, electrolyte concentration, mixing conditions, temperature etc. Therefore detailed study was conducted to find the variations in chemical dose and consequent reduction in optimum chemical dose. And consequent reduction in optimum chemical doses at optimum system P^H conditions determined previously. Variation of color removal at optimum system P^H for Napthal-II dye with varying doses of Alum is given in Table -10 and Graph-4. The maximum 98.47% color removal occurs at chemical dosage of 21 mg/100ml at an optimum P^H of 1.5. Variation of color removal at optimum system P^H for Napthal-I dye varying doses of $AlCl_3$ is given in above table. Table -11 and Graph-5. The maximum 99.79 % color removal occurs at chemical dosage of 2mg/100ml at an optimum P^H of 4. Variation of color removal occurs at optimum system P^H for Vat dye with varying doses of $FeSO_4.7H_2O$ is given in above table. Table -12 and Graph-6. The maximum 51% color removal occurs at chemical dosage of 6mg/100ml at an optimum P^H of 11. There is no significant increase in color removal or reduction in dose requirements even by maintaining optimum P^H conditions. The study clearly indicates that at optimum P^H system conditions, there is significant reduction in the chemical dose requirement. The study also indicates that in some cases a further increase in color removal could be achieved by increasing the chemical dose at optimum system P^H conditions. Therefore in the practical situations a judicious selection of chemical dose requirements would result in either reduced chemical requirements or an increased color removal or even both.

Table- 1 Coagulant vs Napthal-II

Coagulant (1g/100 ml)	Transmitivity (%T)	Optical Density
Alum	97	0.04
$BaCl_2$	69	0.16
$FeSO_47H_2O$	56	0.26
$FeCl_3$	11	0.95
Al_2O_3	49	0.31
$AlCl_3$	84	0.08

Table -2: Napthal-I

Coagulant (1g/100 ml)	Transmitivity (%T)	Optical Density
Alum	86	0.07
$BaCl_2$	21	0.68
$FeSO_47H_2O$	49	0.32
$FeCl_3$	27	0.57
Al_2O_3	68	0.17
$AlCl_3$	72	0.15

Table -3: Vat dye

Coagulant (1g/100 ml)	Transmitivity (%T)	Optical Density
Alum	14	0.86
$BaCl_2$	0	1.00
$FeSO_47H_2O$	27	0.57
$FeCl_3$	18	0.73
Al_2O_3	7	0.93
$AlCl_3$	19	0.71

Table- 4: Napthal-II Vs Alum

Alum (mg/100m)	Transmitivity (%T)	Optical Density
2	97	0.007
6	93	0.02
10	92	0.033
14	89	0.047
16	86	0.053
20	83	0.066
100	66	0.082
1000	10	1.00

Table- 5: Napthal-I Vs $AlCl_3$

$AlCl_3$ (mg/100ml)	Transmitivity (%T)	Optical Density
0.4	96	0.006
0.5	94	0.008
1	91	0.016
2	74	0.034
6	70	0.11
10	67	0.184
16	63	0.204
20	61	0.22
100	53	0.24
1000	27	0.54

Table- 6: Vat dye Vs $FeSO_47H_2O$

$FeSO_47H_2O$ (mg/100ml)	Transmitivity (%T)	Optical Density
2	93	0.007
6	78	0.021
10	81	0.035
14	78	0.051
16	75	0.058
20	72	0.073
100	48	0.091
900	01	1.00

Optimum dosage of coagulant

Table -7: Napthal-II Vs Alum

Alum (mg/100ml)	Transmitivity (%T)	Optical Density	%Color Removal
2	61	0.22	20.6
6	62	0.21	21.1
10	63	0.2	21.65
14	64	0.2	21.65
16	64	0.19	22.16
20	64	0.2	21.65
21	80	0.1	78.39
22	72	0.14	53.6
15	73	0.14	53.6
17	79	0.11	72.16
18	70	0.15	46.91
19	75	0.13	59.79

Table-8: Napthal-I VS $AlCl_3$

$AlCl_3$ (mg/100ml)	Transmitivity (%T)	Optical Density	%Color Removal
2	96	0.02	99.83
6	76	0.12	98.86
10	74	0.14	98.67
14	77	0.12	98.86
16	76	0.12	98.86
20	78	0.11	98.86
0.5	83	0.09	99.14
1.0	82	0.09	99.14
1.5	67	0.18	98.31
2.5	86	0.18	98.31
3.0	80	0.1	99.05
3.5	82	0.09	99.14

Table -9: Vat dye Vs $FeSO_47H_2O$

$FeSO_47H_2O$ (mg/100ml)	Transmitivity (%T)	Optical Density	%Color Removal
2	13	0.87	3.75
6	34	0.47	8.79
10	14	0.84	3.75
14	23	0.62	7.5
16	12	0.93	2.5
20	22	0.63	7.5
3	4	1.36	2.5
4	4	1.31	2.5
5	5	1.27	3.125
7	8	1.06	3.38
8	4	1.34	2.5
9	6	1.24	3.25

Optimum P^H at optimum dosage

Table -10 Napthal-II Vs Alum

P^H	Transmitivity (%T)	Optical Density	%Color Removal
1.5	89	0.05	98.47
2	88	0.05	98.26
3	82	0.08	87.7
4	77	0.11	72.4
7	72	0.14	54
10	70	0.15	46.9
12	68	0.17	34.69

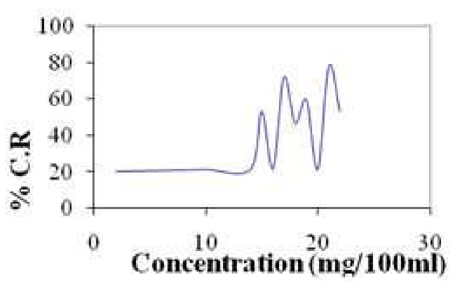
Table -11: Napthal-I Vs $AlCl_3$

P^H	Transmitivity (%T)	Optical Density	%Color Removal
3	94	0.03	99.69
4	96	0.02	99.79
5	94	0.02	99.69
6	91	0.04	99.6
7	88	0.06	99.4
10	81	0.09	99.14
12	85	0.07	99.31

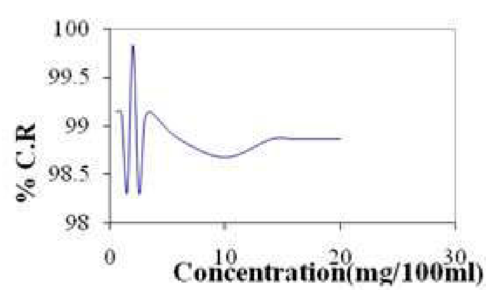
Table -12: Vat dye Vs $FeSO_47H_2O$

P^H	Transmitivity (%T)	Optical Density	%Color Removal
3	20	0.69	3.79
4	28	0.55	6.3
7	31	0.51	6.96
9	49	0.37	17.7
10	41	0.39	13.9
11	51	0.21	26.6
12	34	0.46	10

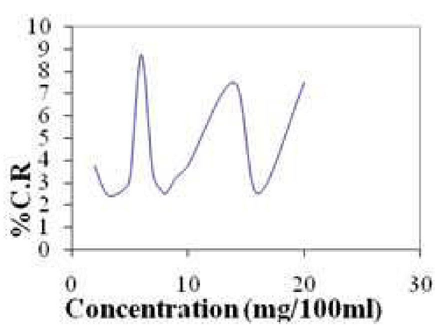
Graph-1 : Napthal-II Vs Alum



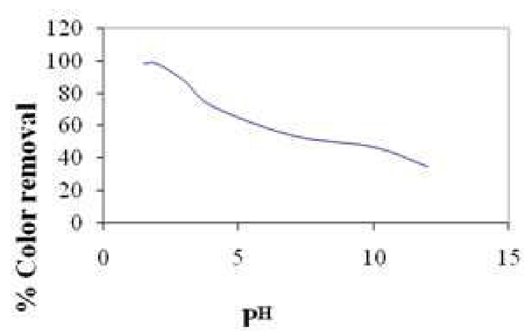
Graph-2:Napthal-I VS $AlCl_3$



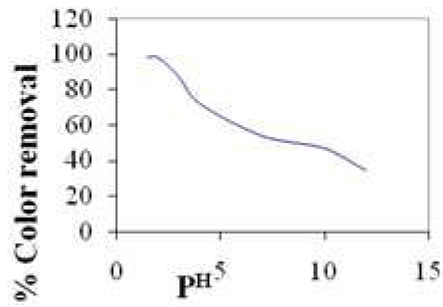
Graph-3: Vat dye Vs $FeSO_47H_2O$



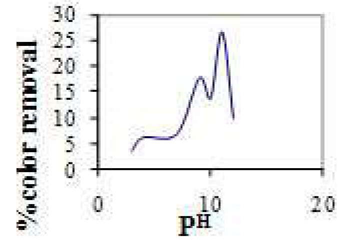
Graph-4: Napthal-II Vs P^H



Graph-5: Napthal-I Vs P^H



Graph-6: Vat dye Vs P^H



CONCLUSION

Some of textile dyes belongs to various application classes and chemical family responded favorably in terms of color removal by chemical treatment with chemical coagulants like Alum, Aluminium Chloride, and Ferrous Sulfate. Influence of P^H on the system found to be significant on color removal. Removal of color was interpreted to be due to specific chemical interactions (chelation/complex formation) between dye ligands and aqua metallic ions resulting in formation of insoluble metal-dye complexes and/or physico-chemical factors like adsorption and interaction between metal hydroxy species and anionic dye aggregates and charge neutralization leading to aggregation. Salient feature being that the optimum chemical dose required at optimum P^H for effective color removal was relatively moderate. The color removal probably due to physicochemical mechanism of coagulation and flocculation and/or chelation complexation type reactions. A perusal of color removal mechanism is predominately physicochemical coagulation especially at alkaline P^H ranges presumably due to adsorption on to hydroxide flocs, and at color removal at lower P^H ranges may be either due to physicochemical coagulation or mainly due to chelation complex formation reactions. The study clearly indicates that at optimum P^H system conditions, there is significant reduction in the chemical dose requirements and in some cases a further increase in color removal. Therefore in the practical situations a judicious selection of chemical dose requirements would result in either reduced chemical requirements or an increased color removal or even both.

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