Fly Ash and Cinder from Coal for the Treatment of Paper Mill Effluents

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SUMMARY

Fly ash and cinder are the wastes produced by the coal fired boilers The quantity of cinder produced in quite enormous, as compared to that of fly ash. Although, work has been reported in literature on the ability of fly ash for the treatment of effluents, the same in the case of cinder has not been found. The paper deals with the investigation on the properties of fly ash and cinder to decolourise alkali extraction effluent which contributes for the dark colour of the paper mill effluents. The laboratory scale experiments revealed that both these solid wastes with the particle size-325 mesh acted as good adsorbents for colour of the effluent. It was also observed that at about 95% colour removal by the adsorbents, 30–40% B.O.D. and 75–85% C.O.D. of the alkali extraction stage effluent could be reduced. The requirement of cinder for removing initial colour of alkali extract effluent of 4000 Pt. Co. units to this extent, was found 50 gm. per litre on the alkali extraction effluent volume. In the case of cinder the conditions like effect of time, pH, temperature, and colour concentration, for maximum colour removal, were optimised. The mechanism of colour removal by the cinder is a complicated phenomenon. The Iodine Number, fixed carbon in the cinder, different metallic radicals present, and the particle size of cinder, did not indicate a definite relationship with the mechanism of colour removal. Our work has indicated that fly ash and cinder may have potential use in the treatment of papk mill effluents.

INTRODUCTION

The effluent treatment and disposal is a problem before every chemical industry including the pulp and paper industry, which needs immediate attention. From toxicity as well as aesthetic point of view the effluent is to be treated and decolourised. The massive lime treatment and activated carbon filters are found to be of considerable improtance for the

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colour removal of effluents ([1], [2]). With the former, the difficulty is in the filtration of the gelatinous precipitate, whereas in latter, high erection cost can not be ignored, at the same time the regeneration technique for the activated carbon has not been successfully developed as yet.

Substantial quantities of fly ash and cinder are produced in pulp and paper industries, where coal is burnt in boiler. The finely divided gas borne matter, resulting from the combustion of pulverised coal is called as fly ash. The refuse or slag of burned coal is called as cinder. The fly ash possesses properties of adsorption and colour reduction of effluents. Considerable work carried out on the adsorption of colour of the effluents by fly ash, has been described in the literature. However, the literatures survey does not describe similar work regarding such properties of cinder. With this view in mind, and also due to easy availability of cinder as a solid waste in paper industry because of coal fired boilers, this project was undertaken. For the first time, work on cinder for the treatment of effluents was carried out and reported by the Research Centre of W.C.P. Mills ([3]).

During conventional bleaching viz. CEHH, the alkali extraction effluent is very dark in colour and contributes to the maximum extent undesirable colour to the mill effluents. This dark colour is mainly due to chlorinated lignin compounds dissolved in sodium hydroxide which are not easily bio-degradable. By removing the colour of alkali extraction effluent, it was anticipated that about 40-50% colour of the total pulp mill effluent will be reduced by this treatment along with some reduction of Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).

EXPERIMENTAL

The representative samples of fly ash and cinder were collected from the Power House of our mill. It was expected that the finer particles would give better adsorption, which was confirmed later experimentally. So these samples were dried and ground to pass through 325 mesh (44 microns). The alkali extraction stage effluent was collected from time to time as per the requirement.

PHYSICAL AND CHEMICAL PROPERTIES

A number of physical and chemical properties of samples of both the materials were determined—moisture content, apparent density, volatile matter, ash content, fixed carbon etc. as per TAPPI standard methods. Particle size distribution was also determined according to Indian Standard 5282-1969. The results are recorded in Table—I, II and IX. The qualitative and quantitative analyses of Ca, Mg, SiO_2 etc. were done according to methods given in literature ([4]).

TABLE — I

PHYSICAL AND CHEMICAL CHARACTERISTICS OF ADSORBENTS

(Composite samples from Power House)

S. No.	Particulars	Fly ash	Cinder
1.	Moisture, %	1.5	1.5
2.	Apparent density, g/cc. (-325 mesh)	0.67	..
3.	Volatile matter, %	14.0	8.9
4.	Ash, %	83.0	76.3
5.	Silica, %	36.6	44.1
6.	pH of water extract	11.05	11.00
7.	Alkalinity Phenol-phthalein, ppm	90.0	75.100
8.	Alkalinity Methyl Orange, ppm	127	110.190
9.	Iodine Number, mg/gm adsorbent	205	196

IODINE—ADSORPTION TEST

This test is recommended by Whittmore for finding out the extent of adsorption ([5]). The Iodine Number is defined as the number of milligrams of iodine adsorbed by one gram of adsorbent when iodine concentration of the residual is 0.02N. One gram of the sample each of fly ash and cinder (passing through 325 mesh) was mixed with 10 ml of 5% HCl and the solution brought to boiling of 30 seconds. After allowing the solution to cool to room temperature, 100 ml of 0.10N iodine solution was added and the solution was shaken vigorously for six minutes. After the shaking period is over the solution was immediately filtered by gravity using Whatman filter paper No. 42. The filtrate was titrated against standard sodium thiosulphate using starch indicator at the end point. The amount of iodine adsorbed was then calculated.

pH AND ALKALINITY OF AQUEOUS SOLUTION

One gram of dried ground adsorbent was shaken vigorously with 200 ml of distilled water for two hours. The slurry was filtered and pH and alkalinity of the filtrate were determined.

COLOUR MEASUREMENT

A stock of standard solution of platinum cobalt with a colour of 500 units was prepared by dissolving 1.246 gm. of Potassium chloroplatinate K_2PtCl_6 (equivalent to 0.50 gm. metallic platinum) and one gm. crystallised cobaltous chloride $CoCl_2.6H_2O$ (equivalent to about 0.25 gm. metallic cobalt), in distilled water with 100 ml concentrated HCl and diluting to one litre by distilled water. By diluting this solution, samples of different colour concentrations (units) were obtained. The absorptions of these solutions were noted on 'Uvispek' Spectrophotometer at a wave length of 400 μ. The absorptions were plotted against the colour units. To determine the colour units of effluents, the absorption values were transferred to platinum cobalt units with the help of calibration graph. The colour was measured at 7.0 pH ([6]).

EFFLUENT TESTING FOR BOD AND COD

Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD) were also determined. The methods used for their determination were according to IS-2488-1966.

OBSERVATIONS AND DISCUSSION

ROLE OF PARTICLE SIZES OF THE ADSORBENTS

The fly ash and cinder possess adsorptive properties which remove the colour and if utlised would help in reducing the colour load of the mill effluents especially that of pulp section of the mill effluent. Cinder and fly ash in the native form, were tried for the reduction in colour of the effluent but failed to give encouraging results. It is well known that by lowering the particle size of the adsorbent, the efficiency of the adsorption increases. Hence, both the adsorbents were ground to pass through 40 to 400 mesh and the effluents were treated with particles of different sizes and the effect of size on the capacity of colour reduction was determined. The results are recorded in Table—II.

TABLE — II

EFFECT OF PARTICLE SIZE OF FLY ASH ON REDUCTION OF COLOUR OF ALKALI EXTRACTION EFFLUENT

Mesh No.		Residual colour, Pt. Co. unit
+ 40	..	2020
—40 + 60	..	1850
—60 + 80	..	1650
—80 + 200	..	1587
—200 + 325	..	650
—325 + 400	..	580
—400	..	540

Fly ash (composite sample) added on effluent = 4.0%
Original colour of effluent = 4500 Pt. Co. units

From this, it was confirmed that lower the particle size of adsorbent, higher will be the reduction in colour. For our experiments, the ground adsorbents passing through 325 mesh were selected, as it removed maximum colour. It was observed that the particle size, finer than this did not further reduce the colour significantly.

PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties of fly ash and cinder were determined. The results are recorded in Table—I.

OPTIMIZATION OF DIFFERENT VARIABLES FOR COLOUR REDUCTION OF ALKALI EXTRACTION EFFLUENT BY CINDER

As mentioned earlier, alkali extraction effluent was found the most suitable for this study as it possesses the maximum colour. The effects of following variables were studied with a view to optimize the conditions.

(i) EFFECT OF TIME : In this experiment, equal quantities of cinder were treated with the same effluent and volumes for different time intervals. It was observed that after 30 minutes, there was no significant change in colour reduction. Hence, for further experiments, treatment was given for 30 minutes. The conditions and results are recorded in Table—III.

TABLE — III

EFFECT OF RETENTION TIME ON REDUCTION OF COLOUR OF ALKALI EXTRACTION EFFLUENT

Time in Min.	5	10	15	30	60	90
Residual Colour, Pt. Co. units	2850	1800	312	285	275	275

Cinder (composite sample) on effluent = 7.0%
Original colour of effluent = 8500 Pt.Co. unit
Temperature = Ambient
pH = as such

(ii) EFFECT OF pH : The pH of the effluent plays an important role in its colour reduction. The values (adjusted by HCl) were treated with adsorbent, effluents with different pH The conditions and results are recorded in Table-IV. From this experiment, it was observed that at lower pH of effluent, the efficiency of adsorbent increased. For the further experiments, the pH of effluent was maintained at 5, as below this pH, there was not much advantage in colour reduction.

(iii) EFFECT OF TEMPERATURE : This experiment was carried out to study the effect of temperature of effluent on reduction in colir by the adsorbent. As the temperature increased, the rate of adsorption of colour also increased

TABLE — IV

EFFECT OF pH OF THE ALKALI EXTRACTION EFFLUENT ON REDUCTION IN COLOUR

pH of the effluent	10.8	9.0	8.0	7.0	5.0	4.0
Residual Colour, Pt. Co. units	1860	1400	1250	1075	800	780

Cinder (composite sample) on effluent = 4.0%
Original colour of effluent = 7000 Pt.Co. unit
Retention time = 30 Min.
Temperature = Ambient

But it is not practicable in commercial practice to treat the effluent at higher temperatures. The temperature of alkali extraction effluent normally remains at 45° C to 50° C. For the further studies the temperature of effluent was maintained at 45° C. The conditions and results of the experiment are recorded in Table —V.

TABLE—V

EFFECT OF TEMPERATURE OF THE ALKALI EXTRACTION EFFLUENT ON REDUCTION IN COLOUR

Temperature of effluent, °C.	29	40	50	55	65
Residual Colour, Pt.Co. units	1800	850	800	770	760

Cinder (composite sample) on effluent = 4.0%
Original colour of effluent = 7000 Pt.Co. unit
Retention time, = 30 Min.
pH = as such

(iv) EFFECT OF COLOUR CONCENTRATION OF THE EFFLUENT : The colour concentration of the effluent itself plays an important role in its treatment with the adsorbent. It was found that, higher the initial colour concentration, higher will be the efficiency of colour removal. This experiment was carried out by taking effluent with different colour concentrations and treated with the adsorbent. The conditions and results are recorded in Table—VI.

At 9000 Pt. Co. units initial colour, the amount of cinder required to remove 95% colour was 10.7 gm. However, at 4000 Pt. Co. units initial colour, it was 6.1 gms. for removing 95% colour. The results

TABLE—VI

EFFECT OF INITIAL COLOUR CONCENTRATION OF ALKALI EXTRACTION EFFLUENT ON REDUCTION OF THE COLOUR

No.	Initial colour of the effluent, Pt.Co. unit	Amount of cinder required for 100 ml of effluent to reduce 95% colour, gm. (Sample X)	Milligram colour bodies removed by 1 gm. of cinder (Sample X)
1	13000	15.5	80.0
2	11000	13.1	80.0
3	9000	10.7	79.5
4	7000	9.1	73.0
5	5000	6.6	72.0
6	4000	6.1	62.5
7	3000	5.1	56.0
8	2000	4.2	45.0
9	1000	2.5	38.0

1 Pt.Co. unit = 1 mg. colouring body.

indicated that the efficiency of colour removal increased upto 9000 Pt. Co. units initial colour and thereafter remained almost constant at higher colour concentration of the effluent. Usually the colour of alkali extraction effluent in our mill is in range of 4000-5000 Pt. Co. units. So far further experiments, alkali extraction effluent of about 4000 Pt. Co. units was taken. In comparison with cinder, the quantity of fly ash produced from Power House is very low, so cinder was taken for further studies. Moreover, the average colour removal efficiency of fly ash was found nearly the same as that of cinder at the particle size below 44 microns. The results are recorded in Table—VII.

REDUCTION OF BOD AND COD FROM EFFLUENTS BY THE TREATMENT OF ADSORBENTS

Apart from the colour removal of the alkali extraction stage effluent by this treatment, reduction in Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) of this effluent were also observed. The conditions and results are recorded in Table--VII.

These results showed that, if the colour reduction of alkali extraction effluent was above 90%, there would be 30-40% reduction in BOD and 75 to 85% reduction in COD. The results are quite comparable to massive lime treatment ([2]). The alkalinity of treated effluent increased significantly due to the considerable amount of basic metallic oxides in the cinder.

TABLE — VII

ADSORPTIVE PROPERTIES OF FLY ASH AND CINDER ON THE PROPERTIES OF TREATED ALKALI EXTRACTION EFFLUENT

Particulars	Alkali Extraction stage effluent	Effluent after treatment with fly ash (4.0%) (Sample F)	Effluent after treatment with cinder (2.5%) (Sample A)	Effluent after treatment with cinder (5.25%) (Sample B)
Iodine Number of adsorbent used, mg./g. adsorbent	..	205	292	270
Std. dye adsorption* Pt.Co. units	..	1050	25	1125
pH	8.5	11.9	11.5	11.9
Alkalinity phenolphthalein, ppm	4	240	186	288
Total alkalinity, ppm	234	306	282	376
Colour, Pt.Co. units	4500	185	100	107
Total dissolved solids, ppm	1685	1609	1383	1343
COD, ppm	790	133	102	88
BOD_5, ppm	108	65	75	78
Reduction in colour, %	..	95.9	97.8	97.6
Reduction in COD, %	..	83.2	87.1	88.9
Reduction in BOD, %	..	40.0	30.5	28.2
Fixed carbon of adsorbent, %	..	8.1	29.0	17.0

* Standard solution of Incomine violet dye was prepared (4000 Pt.Co. unit) by dispersing the dye in water and then filtering the same solution. 2 gms. of adsorbent was taken and then treated with 100 ml dye soln., mixed for 30 minutes at room temperature and the colour of filtrate was determined.

Treatment Conditions :

pH = 5.0
Temp., °C. = 45
Time, Min. = 30

THEORETICAL CONSIDERATIONS

It can be seen from the Table--VIII and IX that the different samples of cinders collected throughout the week possessed different colour adsorptive properties. Hence an attempt was made on some theoretical grounds to find the properties of cinder which make it a very good colour remover. The adsorptive properties combined with chemical reactions of the minerals present in fly ash are responsible for the colour reduction of the effluents. For stydying these adsorptive properties, Whittmore carried out phenol adsorption and iodine number tests of fly ash ([5]). The former being a measure of the activity of adsorbent to adsorb large and "high molecular weight" molecules and the latter, for small and "low molecular weight" molecules.

As there was some practical difficulty in conducting 'Phenol Adsorption Test' in Research Centre, only 'Iodine Number' and 'Standard Dye Adsorption' tests were carried out with different samples of cinders and fly ash. The results are recorded in Table—VIII and IX. It could be visualised from Table—VIII that Iodine Number has given no correlation with

TABLE—VIII

RELATION BETWEEN IODINE NUMBER AND REDUCTION IN COLOUR OF ALKALI EXTRACTION EFFLUENT

Particulars	Iodine Number mg./gm. adsorbent	Residual colour* of alkali extraction effluent, Pt.Co. unit
Fly ash (Sample G)	205	250
Cinder (Sample a)	292	25
Cinder (Sample b)	170	350
Cinder (Sample c)	179	350
Cinder (Sample d)	154	350
Cinder (Sample e)	207	350
Cinder (Sample f)	179	100

* Alkali extraction effluent (colour 4500 Pt.Co. unit) was treated with 5.0% adsorbent.

Time = 30 Min.
pH = 5
Temp. °C. = 45

reduction in colour of the effluent. The presence of lime in the adsorbent imparted false index towards Iodine Number and this was prominent at higher concentration of lime in adsorbent. This is in accordance with the literature(5). The treatment and the colour reduction of standard dye was almost simliar to that of the effluent.

TABLE — IX

COLOUR ADSORPTION PROPERTIES OF DIFFERENT SAMPLES OF CINDER AND FLY ASH

Particulars	Fly ash Sample G	Cinder Sample a	Cinder Sample b	Cinder Sample c	Cinder Sample d	Cinder Sample e	Cinder Sample f	Cinder Sample g	Cinder Sample h
Moisture, %	2.5	2.4	2.2	1.0	1.2	1.2	1.2	1.2	1.2
Ash, %	81.60	62.75	72.23	83.90	81.00	84.05	69.65	72.35	84.95
Volatile matter, %	7.80	5.80	8.60	8.92	9.12	8.78	10.00	11.45	8.42
Fixed carbon, %	8.10	29.55	16.97	6.18	8.68	5.97	19.15	14.00	5.43
Standard dye adsorption test, residual colour, Pt.Co. unit	178	20	165	360	210	272	20	25	500
Residual colour of effluent*, Pt.Co. unit	400	68	..	510	300	295	58	62	1650

* Alkali extraction effluent (5000 Pt.Co. unit colour) was treated with 5% of adsorbent for 30 min. at 5 pH and 45° C. temperature. For standard dye, 2% adsorbent was used, but pH was not changed, temperature was ambient.

The determinations of fixed carbon, volatile matter and ash contents of different cinder samples did not help to clarify the mechanism of colour reduction as there was no correlation between them. The results are recorded in Table—IX. In order to confirm the role of chemical constituents for reducing the colour of effluent the free carbon of the cinder was burnt and the ash was used as an adsorbent and the effluent was treated with this. The results are recorded in Table—X. This experiment showed that ash of cinder sample No. III and to some extent cinder sample No. IV were different than other cinders i.e. sample Nos. I, II, V and VI. Samples of ash of the first group i.e. III and IV, removed the colour of alkali effluent appreciably, as compared to those of the others i.e. I, II, V and VI. It was suspected that the presence of different chemicals, their combinations and concentrations might be responsible for this difference. So the chemical analysis of one cinder from each group (I and III) was carried out. The results are recorded in Table — XI. This analysis could not confirm the above idea. At this stage, it was thought that variations in the amounts of very fine particles might be responsible for the differences in the adsorptive properties of cinder samples. Therefore, the determination of particle size by sedimentation method was carried out. However, this also did not help to draw definite conclusions. The results of the experiments are recorded in Table — XII.

TABLE—X

EFFICIENCY OF ASH OF CINDER SAMPLES FOR THE REMOVAL OF COLOUR

Particulars	Residual colour of standard dye solution,* Pt.Co. unit	Residual colour of alkali extraction effluent,** Pt.Co. unit
Ash of Cinder Sample I	1500	4025
Ash of Cinder Sample II	1400	4000
Ash of Cinder Sample III	1150	1475
Ash of Cinder Sample IV	1170	2850
Ash of Cinder Sample V	1400	3900
Ash of Cinder Sample VI	1500	4025

* Standard dye solution (4000 Pt.Co. unit-colour) was treated with 2.0% adsorbent for 30 minutes.
** Alkali extraction effluent (4300 Pt.Co. unit-colour) was treated with 2.0% adsorbent for 30 minutes at pH 5 and temp. 45° C.

It appeared that the above mentioned properties contribute for the reduction in colour of the effluents either individually or collectively. However, correlation between any of the properties and reduction in colour could not be confirmed. In order to establish the correlation between adsorptive properties and

TABLE—XI

ANALYSIS OF ASH FROM CINDER
(Constituents of ash expressed in percent)

No.	Particulars	Ash from cinder (Sample I)	Ash from cinder (Sample III)
1.	SiO_2	58.30	57.60
2.	R_2O_3 (Fe. Al.)	29.50	28.60
3.	Ca	4.33	4.65
4.	Mg	2.40	2.42

Pt. Co. units as stated earlier. For this colour range, 50 gm. of cinder per litre effluent, would be required to reduce 95% colour alongwith reduction of 30-40% BOD and 75-85% COD. So on this basis, it is possible to calculate the amount of cinder required to the reduction of the colour, BOD and COD of alkali extraction as per the pulp production and volume of the effluent.

CONCLUSIONS

(1) The laboratory experiments revealed that fly ash and cinder obtained as wastes from coal fired boilers were effective for the treatment of the effluents for reducing 90-95% colour, Biochemical Oxygen Demand (BOD) to the extent of 30-40% and Chemical Oxygen Demand (COD) to the extent of 75-85%.

TABLE — XII

PARTICLE SIZE DISTRIBUTION OF GROUND CINDER BY SEDIMENTATION METHOD

Particle mean size, Microns	Cinder Sample IV	Cinder Sample I	Cinder Sample V	Cinder Sample VI	Cinder Sample III	Cinder Sample II	Cinder Sample VII
44.8	62.25	45.38	31.65	38.13	72.13	38.98	35.76
37.8	26.44	47.05	52.84	44.00	13.25	39.57	51.74
26.3	6.50	4.56	11.87	9.81	3.72	15.22	9.81
Total coarser particles, %	95.89	96,99	96.36	91.94	89.10	93.77	97.31
18.4	0.47	1.72	1.74	1.59	1.42	5.22	2.21
12.6	0.79	0.43	1.58	5.06	6.30	0.23	0.48
<10	2.85	0.86	0.32	1.41	3.18	0.78	2.69
Total finer particles, %	4.11	3.01	3.64	8.06	10.90	6.23	2.69
Reduction in colour of effluent, %	99.04	98.50	91.00	84.50	56.00	48.20	36.20

Table is arranged to show the effect of reduction in colour of alkali extraction effluent from maximum to minimum.
All the results are expressed in percentage.

other physical and chemical properties of cinder, further detailed experiments are planned along with experiments on sludge handling. At the same time experiments are also being planned to increase the effectiveness of the adsorptive properties of the cinder for optimisation of particle size so as to consume less quantity of adsorbent for effluent treatment, and less energy consumption in grinding etc.

INDUSTRIAL APPLICATION

As these cinder samples vary in their adsorptive properties, the average quantity of cinder required to reduce 95% colour of alkali extraction stage effluent was determined by collecting representative samples for a week. Usually the colour of alkali extraction stage effluent in our mill is in the range of 4000-5000

(2) The treatment of effluent with fly ash and cinder was found effective when it was powdered to pass through 325 mesh (44 microns).

(3) At higher temperature and pH 5, retention time of 30 minutes was found sufficient for the treatment of the effluent.

(4) At higher initial colour concentration (not more than 9000 Pt. Co. units) of effluent, the effectiveness of cinder was found higher and after 9000 Pt. Co. units effectiveness of cinder did not improve.

(5) None of the physical or chemical properties, which were studied were found to have straight relationship with the adsorptive properties of cinder or fly ash.

(6) The effectiveness of adsorptive property varies with the quality of cinder.

ACKNOWLEDGEMENT

The authors are very much thankful to the Management of M/s. The West Coast Paper Mills Ltd. for their kind permission to publish this paper.

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