Journal of Basic and Applied Engineering Research
p-ISSN: 2350-0077; e-ISSN: 2350-0255; Volume 5, Issue 5; July-September, 2018, pp. 400-404

http://www.krishisanskriti.org/Publication.html

Studies for Use of Coal Fly Ash and Rice Husk Ash for Colour Removal of Pulp and Paper Mill Effluent

Divya Bisht[1], Rachna Singh[2] and R.K. Jain[3]

[1]Senior Scientist, Centre for Fly Ash Research and Management (C-FARM) and Research Fellow, Amity Institute of Biotechnology, Amity University, Noida
[2]Professor, Amity Institute of Biotechnology, Amity University, Noida
[3]Ex Director, CPPRI, Saharanpur
E-mail: [1]divyab116@gmail.com, [2]rsingh2@amity.edu, [3]rkjain_knhpi@yahoo.co.in

Abstract—*Pulverised coal ash generated at Thermal Power plant is a waste material. The morphology of fly ash particles as well as the present unburnt carbon imparts good adsorption property to fly ash. The small and medium size agro-based pulp and paper mills are in need of appropriate and affordable technology to bring down the colour of effluent discharged after secondary/ tertiary treatments to the levels acceptable to Central Pollution Control Board. Rice husk ash another abundantly available low cost material is also reported to have good adsorption properties. Detailed investigations are undertaken for colour removal of agro-based pulp and paper mill effluent using coal ash as well as rice husk ash varying the dose, interaction intensity, interaction time, pH and temperature etc. The technology has been optimised to reduce the colour intensity from 978 PCU to below 100 PCU the environmental requirement for discharge into water bodies and also for reuse.*

Keywords*: Colour removal, pulp and paper mill effluent, adsorption, fly ash, rice husk ash, clean technology.*

1. INTRODUCTION

Paper industry is one of the high priority industries having a bearing on the socio-economic development of the country. It provides necessary medium to propel the knowledge based economy forward. The Indian paper industry is adopting new technologies at a fast pace to be of international standards and quality. The average growth rate of this industry is around 6.5% with current annual turnover of about Rs. 500 billion. Even with the sustained growth, Indian paper industry contributes only around 4% of the global production of this sector [7]. The per capita consumption of paper in India is quite low at about 13kgs in comparison to global average of 57kg, China's average of 74 kg and 200 kg in North America. Large size mills that use wood as the raw material are employing the latest technologies. With only 4% in number of the total pulp and paper mills, these big mills contribute to about 35% of the paper production in India. 12% of pulp and paper mills using agro-residue as the feed stock contribute to about 25% of the industry production. These mills are of small capacity and spread spatially. Rest of the mills are primarily using recycled fibre and waste paper etc. The effluent of agro-residues based mills even after primary and secondary treatments is characterized with high colour intensity. The effluent due to its colour can neither be discharged into the water bodies nor reused. The pressures on water availability mandate re-use of waste waters.

These mills are in search of appropriate affordable technologies to mitigate the colour menace in the effluent.

2. LITERATURE REVIEW

One of the major issues is the persistent dark brown colour of effluent even after secondary treatment. This is primarily due to lignocellulosic and its derivatives, such as chlorolignin in the effluent discharged from the pulp bleaching process [8]. The effluent causes considerable damage to the receiving water and is hazardous to aquatic life if discharged untreated since, they have a high Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and a low biodegradability (defined as the ratio of BOD5/COD) and more than 200 different organic and inorganic compounds [6]. These include non-biodegradable organic materials, chlorinated compounds measured as adsorbable organic halogens (AOX), colour, phenolic compounds, suspended solids mainly fibres, fatty acids, tannins, resin acids, lignin and its derivatives, sulphur and sulphur compounds, etc. [2], depending upon the applied pulping process, additive chemicals, wood material, process technology, recirculation of the wastewater for recovery of chemicals and the amount of water consumed.

There are different techniques to treat the pulp and paper mill effluent. Physicochemical treatment processes are being generally employed by the industry. These include removal of suspended solids, colloidal particles, floating matters, colours and toxic compounds by sedimentation, flotation, screening, adsorption, coagulation, oxidation, ozonation, electrolysis, reverse osmosis, ultra-filtration and nano-filtration technologies [3, 9, 11]. However methods like coagulation with lime or iron salts, ultrafiltration etc. have also not been very effective for color removal of pulp & paper mills

effluents. And these processes are quite expensive and are generally considered to be commercially nonviable for small and medium size mills [4]. Adsorption by activated carbon is the most widely used process for color removal of industrial effluent but the high cost and tedious procedure for the preparation and regeneration of activated carbon is a limitation for its use for pulp & paper mills. There is a continuous search to find out low-cost adsorbent material for removing colour of effluent of this industry.

Biological treatment methods with utilization of microbes including fungi, bacteria, algae and enzymes, as a single step treatment or in combination with other physical and/or chemical methods have been reported [12]. But these have also not provided the required solution. Further research is needed to develop fast biodegradation processes which are likely to provide an economically feasible process [5].

On the other hand Coal-based thermal power plants all over the world face serious problems of handling and disposal of the ash produced. The high ash content (30–50%) of the coal in India makes this problem complex. At present, about 110 thermal power stations produce nearly 240 million tonne of coal ash per annum. Safe disposal of the ash without adversely affecting the environment and the large storage area required are major concerns.

Fly ash, a waste material produced from the combustion of coal in thermal power plants has also been used by many researchers for wastewater treatment for the removal of heavy metal ions from aqueous solutions [1]. It has been reported [10] that bottom ash adsorbs heavy metal. Many researchers have investigated fly ash as an adsorbent for the removal of phenolic compound, heavy toxic metals, dyes, organic pollutants and organic acids from industrial effluents. However, optimized solution has not been established.

3. MATERIALS AND METHODS

Pulp and paper mill effluent

Effluent is collected from a pulp and paper mill in Southern area of Uttarakhand using agro-residues as the feed stock and is collected after the secondary treatment.

Coal fly ash. Coal fly ash is collected from a thermal power plant located in Western U.P.

Rice Husk Ash. Rice husk ash is collected from the captive power plant of a pulp and paper mill using Rice husk as the fuel.

Characterisation of pulp and paper mill effluent. Color of effluent was determined by spectrophotometer. For determining TSS, the sample of effluent is filtered through a standard filter and the mass of the residue is used to calculate TSS. Total solids (TS) are found by evaporating the effluent at a specified temperature. TDS is then calculated by subtracting TSS from TS. COD is determined by dichromate reflux method. BOD is determined by the 5-day biological oxygen demand (BOD5). DO, total alkalinity, total acidity, chloride analysis carried out as per standard methods.

Characterization of coal fly ash. Coal fly ash is characterized as per the protocols prescribed in IS-3812.

Characterization of Rice husk ash. Rice husk ash is also characterized as per IS-3812. There is no other standard or protocol for rice husk ash characterization.

4. EXPERIMENTS

Effluent is treated with coal fly ash and rice husk ash separately by varying the (i) dose of adsorbent (ash) from 10 gm/lt to 90 gm/lt in steps of 10 gm, (ii) interaction time from 10 minutes to 90 minutes in steps of 10 minutes and (iii) intensity of interaction from 10 oscillations to 100 oscillations per minutes. The mixture of effluent and the ash are allowed to sediment till the effluent on the top is near transparent clarity. Poly-aluminium chloride (PAC) based coagulant; non-reactive is used to hasten the process of sedimentation. The decanted effluent is analyzed and measurement of colour intensity is recorded.

5. EQUIPMENT

The Spectrophotometer (LAMBDA XLS$^+$ by Perkin Elmer) was used for colour measurement. The shaker (Thermo Scientific Max Q 3000), magnetic stirrer (Remi-5MLH), pH meter (SPECTRA-Digital), Centrifuge machine (Labline S-103), etc. were used for all adsorption experiments.

6. RESULTS AND DISCUSSIONS

The chemical and physical analysis of coal fly ash and rice husk ash is given in table 1 and 2.

Table 1: Chemical Analysis of Coal Ash and Rice Husk Ash

Sl. No	Parameter	Unit	Coal Fly Ash	Rice Husk Ash
1.	Total Silica (SiO2) + Aluminium (Al2O3) + Iron (Fe2O3)	%	89.20	85.27
2.	Total Silica (SiO2)	%	57.10	84.80
3.	Aluminium Oxide (Al2O3)	%	26.47	0.28
4.	Iron Oxide (Fe2O3)	%	5.63	0.19
5.	Calcium Oxide (CaO)	%	1.91	1.60
6.	Magnesium Oxide (MgO)	%	2.34	0.70
7.	Sulphur Trioxide (SO3)	%	0.70	0.95
8.	Available Alkali as Na2O	%	0.95	0.60
9.	Unburnt Carbon	%	1.93	8.80
10.	Chromium as Cr	ppm	20.60	5.60
11.	Cadmium as Cd	ppm	0.34	BDL
12.	Mercury as Hg	ppm	BDL	0.056
13.	Arsenic as As	ppm	BDL	BDL
14.	Selenium as Se	ppm	BDL	BDL
15.	pH		8.1	8.5

Table 2: Physical Analysis of Coal Ash and Rice Husk Ash

Sl. No.	Parameters	Coal Fly Ash	Rice husk ash
1.	Specific Gravity	2.60	1.86
2.	% Material Below (Nearest per cent value)		
	1 µ	0.15	13
	2 µ	0.23	18
	5 µ	2.10	29
	10 µ	5.20	53
	25 µ	18.00	75
	45 µ	50.00	84
	75 µ	85.00	90
	100 µ	97.00	91.5

The colour removal effectiveness is pronounced in the adsorbent dose range of 40 gm/lt to 80 gm/lt with the interaction time of 40 to 80 minutes and at interaction intensity of 60 to 90 oscillations/ minute. The colour intensity of the effluent as collected from pulp and paper mill is 978 PCU. The resultant colour of pulp and paper mill effluent after treatment with coal fly ash and rice husk ash with combination of various operating parameters is given in table 3(a) to 3 (d) and 4 (a) to 4 (d)

Table 3: Colour of Effluent after treatment with coal fly ash

a) 60 oscillation/minutes

(PCU)

Dose (gm/lt) → / Time (min) ↓	40	50	60	70	80
40	736	510.4	328.4	345.6	360.8
50	642.4	351.2	254.4	302.4	329.2
60	446	304.8	220.8	255.2	278.4
70	476.4	275.6	240	282	306
80	520	303.2	263.6	314.4	335.6

b) 70 oscillation/minutes

(PCU)

Dose (gm/lt) → / Time (min) ↓	40	50	60	70	80
40	711.2	497.6	292.8	302.8	338.4
50	617.2	335.6	159.6	178.4	201.2
60	421.6	182.4	132.4	147.2	158.4
70	456.8	214.4	135.2	155.6	171.2
80	495.6	254.4	150	180.4	196.4

c) 80 oscillation/minutes

(PCU)

Dose (gm/lt) → / Time (min) ↓	40	50	60	70	80
40	676.4	437.8	260.4	276.8	297.6
50	589.4	315.6	134	152.4	173.6
60	410	153.8	86.8	103.6	120
70	445.2	171.2	100.6	122	130.8
80	464.8	203.6	122.4	142.8	150.4

d) 90 oscillation/minutes

Dose (gm/lt) → / Time (min) ↓	40	50	60	70	80
40	700.4	486.8	289.2	303.2	338
50	613	332.8	158	175.2	201.2
60	410.4	178	123.2	136	148.8
70	448	206.4	137.6	151.2	165.2
80	482.8	248.8	144.8	168.8	192.4

Table 4: Colour of Effluent after treatment with Rice husk ash

a) 60 oscillation/minutes

(PCU)

Dose (gm/lt) → / Time (min) ↓	40	50	60	70	80
40	881	450.4	440.4	460.60	465.6
50	792.4	466.2	371.4	427.4	469.2
60	596	432.8	335.8	402	414.4
70	600.4	400.6	405.6	400	445.6
80	648	425.2	383.6	432.4	459.6

b) 70 oscillation/minutes

(PCU)

Dose (gm/lt) → / Time (min) ↓	40	50	60	70	80
40	859.2	532.6	402.8	451	470
50	767.8	450.8	260.2	275.2	340.3
60	570.5	303.5	250.1	258.4	270.1
70	601.1	340	240.2	262.1	290.3
80	624.3	385.5	280.1	301.8	215.3

c) 80 oscillation/minutes

(PCU)

Dose (gm/lt) → / Time (min) ↓	40	50	60	70	80
40	825.4	567.8	370.4	391.8	398.3
50	734.4	439.6	234	260.4	287.6
60	555	270.3	187.8	140.1	160.2
70	594.2	281.2	205.3	230	235.3
80	614.8	324.3	223	250.3	260.2

d) 90 oscillation/minutes

(PCU)

Dose (gm/lt) → / Time (min) ↓	40	50	60	70	80
40	845.6	613.2	399.2	415.2	451.2
50	760	439.8	259	287.2	317.3
60	556.1	298	224	252	260.8
70	586	331.2	257	270.2	285.3
80	631.3	371.9	258.2	280	303.2

The treatment with coal fly ash is very effective and reduces the colour below 125 PCU to meet the requirements of CPCB in table 3 (c). The optimum parameters are (i) coal fly ash dose of 40 to 80 gm/lt, (ii) interaction time of 60 to 80 minutes and (iii) interaction intensity of 80 oscillations/ minutes. Colour intensity of 123.2 PCU is also achieved with 60gm/lt dose and interaction time of 60 minutes at 90 oscillations/ minute interaction intensity table 3(d). The observations reported in tables 3&4 are average of 5 series of trials. Treatment of effluent with rice husk ash ash is also effective but to a lesser degree than coal fly ash. The un-burnt carbon in the rice husk ash is imparting black colour to the effluent. The particles of rice husk ash being light in weight, take much larger time to settle down, thus imparting haziness to the effluent. Even addition of extra dose of coagulant and waiting for additional 30-60 minutes for sedimentation of rice husk particles, the imparted black colour did not subside. This appears to a cause for the colour of treated effluent not getting reduced below 140 PCU and generally remaining above 200 PCU table 4 (c) & (d).

The effluent treated with coal fly ash achieving colour intensity of below 100 PCU is analysed for various properties vis-à-vis that of untreated effluent. Table 5 presents the analysis results.

Table 5: Analysis of effluent before and after treatment

Sl. No	Parameter	Unit	Before Treatment	After Treat-ment
1.	BOD	ppm	86	26
2.	COD	ppm	596	167
3.	TSS	ppm	197	97
4.	TDS	ppm	1236	1260
5.	DO	ppm	6	6
6.	Chlorides	ppm	845	815
7.	pH		8.2	8.2
8.	Electrical Conductivity	dS/m	2.56	2.85
9.	Color	PCU	978	95
10	AOX	mg/l	4.72	1.34
11	Chromium as Cr	ppm	0.005	0.005
12	Phosphate as P	ppm	0.33	4.30
13	Sulphate as SO4	ppm	1223	1278
14	Total Acidity as CaCO3	ppm	1514	1207
15	Cadmium	ppm	BDL	BDL
16	Cobalt	ppm	BDL	BDL
17	Mercury	ppm	BDL	BDL
18	Arsenic	ppm	BDL	BDL
19	Selenium	ppm	BDL	BDL
20	Lead	ppm	0.001	0.001
21	Nickel	ppm	BDL	BDL

The coal fly ash in addition to reduction of colour of the pulp and paper mill effluent has positive impact on reduction of BOD, COD, TSS, Chlorides and a few other parameters.

7. CONCLUSION

Based on the research work, it can be concluded that coal fly ash generated by thermal power plants can be gainfully applied for treatment of agro residue based pulp and paper mill effluent for colour removal after primary and secondary treatment. It makes waste water re-usable reducing the demand of fresh water. Treatment of effluent with rice husk ash also reduces the colour intensity however, rice husk ash imparts black colour to the effluent.

REFERENCES

[1] Alinnor, I. J. and Nwachukwu, M. A., "A Study on removal characteristics of para-nitrophenol from aqueous solution by fly ash", *Journal of Environmental Chemistry and Ecotoxicology*. 3 (2), 2011, pp. 32-36.

[2] Buyukkamaci, N. and Koken, E., "Economic evaluation of alternative wastewater treatment plant options for pulp and paper industry", *Science of the Total Environment*, 408: 2010, pp. 6070-6078.

[3] Dey, S., Choudhury M. D. and Das, S., "A review on toxicity of paper mill effluent on fish", *Bulletin of Environment Pharmacology and Life Sciences*, 2, 2013, pp. 17-23.

[4] Gutierrez, A., Rodriguez, I. M. and Del Rio, J. C., "Chemical characterization of lignin and lipid fractions in industrial hemp bast fibers used for manufacturing high-quality paper pulps", *Journal of Agricultural and Food Chemistry*, 54, 2006, pp. 2138-2144.

[5] Hossain, K. and Ismail, N., "Bioremediation and Detoxification of Pulp and Paper Mill Effluent: A Review", *Research Journal of Environmental Toxicology*, 9, 2015, pp. 113-134.

[6] Karrasch, B., Parra, O., Cid, H., Mehrens M. and Pacheco P., "Effects of pulp and paper mill effluents on the microplankton and microbial self-purification capabilities of the Bibyo River, Chile", *Science of the Total Environment*, 359: 2006, pp. 194-208.

[7] Planning Commission of India, Working Group for interventions to accelerate the growth during twelfth plan period (2012-2017).

[8] Prasongsuk, S., Lotrakul, P. Imai T. and Punnapayak, H., "Decolourization of pulp mill wastewater using thermotolerant white rot fungi", *Science Asia*, 35, 2009, pp. 37-41.

[9] Sharma, P., Goel, R. and Capalash, N., "Bacterial laccases", *World Journal of Microbiology and Biotechnology*, 23, 2007, pp. 823-832.

[10] Shim, Y. S., Kim, Y. K., Kong, S. H., Rhee, S. W. and Lee, W. K., "The adsorption characteristics of heavy metals by various particle sizes of MSWI bottom ash", *Waste Management*, 23 (9), 2003, pp. 851–857.

[11] Singh, Y. P., Dhall, P., Mathur, R. M., Jain, R. K. and Thakur, V. V., "Bioremediation of pulp and paper mill effluent by tannic acid degrading *Enterobacter* sp.", *Water Air Soil Pollution*, 218, 2011, pp. 693-701.

[12] Singhal, A. and Thakur, I. S., "Decolorization and Detoxification of Pulp and Paper Mill Effluent by Cryptococcus sp.," *Biochemical Engineering Journal* 46 (1), 2009, pp. 21-27.