Characterization and Comparative Study of Fly ash from Various Sources for its Sustainable Utilization

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ABSTRACT

Fly ash is a waste product generated from various sources in very large quantities around the globe. Effective utilization of fly ash which not only reduces disposal problems but also leads to sustainable development. In this study, characterization of five different fly ash samples was performed using Brunauer–Emmett–Teller (BET), X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Thermo-gravimetric Analysis (TGA) techniques. The presence of SiO_2, Al_2O_3 and CaO as the major constituents and irregular surfaces of fly ash support adsorption process. The comparative study of fly ash samples showed various characteristics depending on the source of the sample and environmental conditions. Sample collected from sugar factory was found to have comparatively more surface area and good adsorption property. Hence it can further be utilized for the pre-clean up treatment of samples having diverse nature.

Keywords: Fly ash, Sustainable development, Characterization, Adsorption

I. INTRODUCTION

Coal is the major source of energy in India and nearly hundred million metric tons of fly ash is generated annually by burning of coal from factories and several thermal power plants. Hence, the disposal of such a huge quantity of fly ash is the major environmental concern. Ash produced from such factories and thermal power plants is dumped in landfills and ash ponds. Due to the shortage of landfill sites, increasing costs of the land and strict environmental regulations, the disposal of fly ash has become a major issue. This also creates many environmental hazards if not managed well and causes soil pollution and ground water pollution [1]. In the recent few years, many studies have investigated effective ways to utilize fly ash for valuable applications such as manufacturing of bricks and building blocks, sintered aggregates, pozzolana cement, concrete, filler material for reclamation of low lying waste lands, filling of mines, improvement

of foundation soils, asphalt concrete, as a stabilizer of sub-grade and sub-bases in pavement construction and zeolite synthesis for waste water treatment [2,3]. Fly ash has potential use in waste water treatment as it fulfils the physical properties of adsorption like porosity, surface area and particle size distribution. The presence of major chemical components like silica, alumina, calcium oxide, magnesium oxide and carbon also contribute towards its use as a good adsorbent [4]. Now a days sustainable development and natural resources preservation have gained significant importance. Hence, utilization of fly ash not only alleviates the disposal problem but also converts a waste material into a marketable commodity [5,6]. Characterization of fly ash in terms of composition and surface chemistry is of fundamental importance in the development of various applications of fly ash related to its adsorption property [7]. A comparative analysis of characteristics of fly ash collected from different sources could generate more information

regarding its utilization in areas other than its regular applications. This paper describes a comprehensive study of five different samples of fly ash, with the intention of elucidating their chemical and physical properties as an incentive to their sustainable utilization of adsorption property.

II. METHODS AND MATERIAL

A. Fly ash collection and adsorbent preparation:

1) Samples:
1. Sugar Factory Sample 1 (SF1)
2. Sugar Factory Sample 2 (SF2)
3. Thermal Power Plant (TPP)
4. Wood Ash (WA)
5. Foundry (FOU)

All the fly ash samples were sieved through ASTM 45 mesh, treated with distilled water to remove all adhering dust particles and organic matter, dried in an oven at 110^0C and were stored in labelled polyethylene terephthalate (PET) bottles at room temperature.

B. Characterization of Fly ash:

Proximate analysis which includes pH test (DBK Digital pH meter), specific gravity (Using Pycnometer), Bulk density, Moisture content, Loss on Ignition (LOI) were performed.

In order to characterize and compare the utility of the fly ash samples they were subjected to Scanning Electron Microscopy (SEM) (FEI QUANTA 200), to study the morphological features and characteristics, Brunauer–Emmett–Teller (BET) (Smart Sorb 92/93), for specific surface area calculations, X-Ray Fluorescence (XRF) (Shimadzu,EDX 7000), for knowing the composition, Fourier Transform Infrared Spectroscopy (FTIR) (Shimadzu IRAffinity-1), for functional group study and Thermo-gravimetric Analysis (TGA) (METTLER STAR^{0}SW 12.10) to check the thermal stability of the samples.

C. Batch adsorption study:

To analyse adsorption property and effectiveness of fly ash, a representative batch adsorption study was performed by considering Indigo carmine dye (supplied by Molychem) as an adsorbate. The parameters such as dye concentration, amount of adsorbent, pH, temperature and contact time, were optimized by varying all the conditions within a defined range using the One-FactorAt-A-Time approach. Known amount of adsorbents with 25 cm^3 of known concentration of dye solution was taken in 50 cm^3 of Erlenmeyer flasks. These flasks were agitated in orbital shaker. (Pooja lab equipments orbital shaker cum incubator OSI-200) The pH of the solution was adjusted by 0.1 N NaOH or HCl. Once the equilibrium was established, supernatant liquid was filtered off using Whatman filter paper no. 41 and the filtrates were analyzed for the residual (unadsorbed) dye, spectrophotometrically. (Shimadzu UV-1650 PC) Calibration curve was plotted of absorbance Vs. concentration of standard dye solutions.

The amount of dye adsorbed at time t, qe (mg/g), was obtained by calculating the difference between the initial and the final dye concentration as shown in equation 1:

$$qe=(C_0-Ce)\times V/W \qquad (1)$$

Where qe is the amount of dye adsorbed (mg/g) and C_0 is the initial dye concentration (mg/L), while Ce is the concentration of dye in solution at equilibrium (mg/L), V is the volume (L), and W is the weight of adsorbent(g).

The percentage removal of the dye was computed using the following equation

$$\text{Percentage of removal (\%)} = (C_0-Ce)\times 100/C_0 \qquad (2)$$

Where C_0 and C_e are the initial and equilibrium concentration of dye (mg/L) in solution [8].

III. RESULTS AND DISCUSSION

A. Proximate analysis: The results of proximate analysis are mentioned in Table 1. The specific surface area and LOI of SF1 was high when compared with the other samples. The presence of unburned carbon in fly ash changes its color to black and appears to be responsible for the adsorption process [9]. The specific gravity values for fly ash range between 1.70 and 2.43. In general, the bulk density, pH and moisture content values recorded did not show significant variations.

Table 1. Proximate analysis of Fly ash samples

Samples	SF1	SF2	TPP	WA	FOU
Color	Tan	Grey	Grey	Grey	Brown
Bulk density (gcm^{-3})	1.224	1.213	1.308	1.021	1.332
Specific gravity (gcm^{-3})	1.804	2.285	1.706	2.290	2.430
Moisture content (%)	0.027	0.004	0.001	0.009	0.004
pH	8.6	9.2	7.5	10.9	8.6
LOI (%)	1.039	0.231	0.079	1.199	0.466
BET (m^2g^{-1})	51.96	10.94	2.04	29.15	2.77

B. Scanning Electron Microscopy (SEM): In the present study, majority of particles were found to be of irregularly shaped. The surface tends to be more rough and uneven, which is favours/beneficial for adsorption (Fig 1) [10].
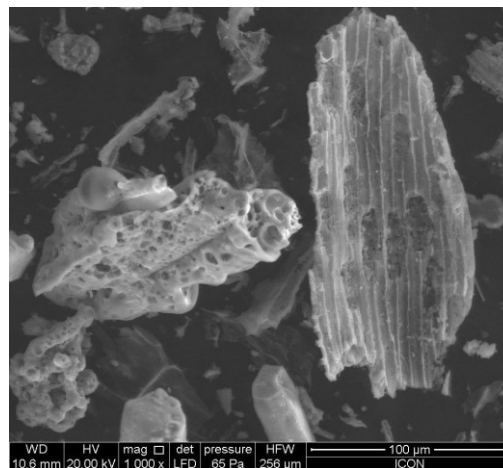

Figure 1. Representative SEM image.

C. X-Ray Fluorescence (XRF): The details of the chemical constituents in the samples determined by XRF are provided in Table 2. It shows the presence of major constituents as SiO_2, Al_2O_3 Fe_2O_3, MgO, CaO and K_2O. Similar constituents of fly ash were obtained by others [4,8].

Table 2. XRF Analysis

Analyte	SF1(%)	SF2(%)	TPP(%)	WA(%)	FOU(%)
SiO_2	75.821	81.518	61.230	23.805	54.892
Al_2O_3	0.538	0.578	26.088	1.500	19.031
MgO	2.399	3.207	0.711	7.434	2.659
SO_3	2.030	0.222	0.088	1.723	4.237
CaO	4.829	3.867	1.412	28.262	6.272
Fe_2O_3	1.734	1.172	6.553	2.852	7.982
TiO_2	0.259	0.163	2.113	0.404	1.923
K_2O	6.766	6.162	1.280	25.175	1.172
CuO	0.035	0.012	----	0.046	0.787
ZnO	0.017	0.026	0.010	0.069	0.348
MnO	0.080	0.076	0.076	0.139	0.176
PbO	----	----	----	----	0.111
V_2O_5	0.015	----	0.069	----	0.096
ZrO_2	0.003	0.002	0.065	----	0.066
SnO_2	----	----	----	----	0.058
Cr_2O_3	0.012	0.009	0.024	0.297	0.056

SrO	0.026	0.021	0.037	0.080	0.056
P_2O_5	2.258	2.963	0.239	3.663	0.051
NiO	----	----	----	----	0.026
NbO	----	----	0.004	----	----
Cl	3.181	----	----	4.552	----

D. Fourier Transform Infrared Spectroscopy (FTIR): The FTIR technique is an important tool to identify same characteristic functional groups. By comparing the observed frequencies with available literature, following interpretation could be drawn. A strong peak in the region 1200-900 cm^{-1} is typical of the glassy phase in fly ash which is the main provider of Si and Al sources. This vibration band in this region varies with different Si to Al ratios and Ca content. The presence of Si–O–Si stretching vibration in this region was observed in all the samples. The peaks between 794-777 cm^{-1} in SF1, SF2 and TPP samples could be assigned to the presence of quartz with Si–O symmetrical stretching vibrations. The peaks in WA sample at around 711 cm^{-1} and 873 cm^{-1} could be assigned to carbonate group (C-O bending) of calcite. The midinfrared region (1500–1400 cm^{-1}) of the spectra of WA sample is dominated by the vibrational modes of carbonate ions (C-O stretching) (Figure 2) [11,12].
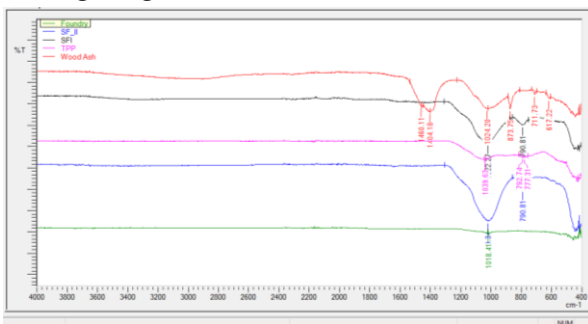

Figure 2. FTIR Spectra

E. Thermogravimetric Analysis (TGA): The initial loss in all the samples is related to the loss of adsorbed moisture. The weight loss between 550^{0}C to 650^{0}C in WA and FOU samples could be due to the thermal decomposition of Acetate.

There is a presence of broad peak between750^{0}C to 950^{0}C in the WA sample and that could be of $CaCO_3$ [13]. Rest all other samples did not show any major loss (Figure 3).
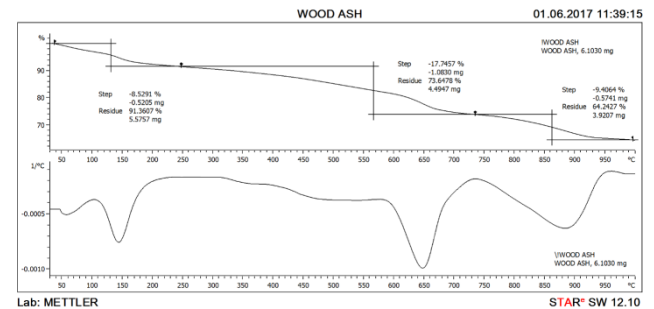

Figure 3. Representative TGA

F. Sorption study:

1) Effect of contact time:

Various contact times ranging from 20 to 60 minutes were considered to study the effect of contact time. The amount of dye adsorbed on to the sample was calculated at each time interval and it was found that as the contact time increases the amount of dye adsorbed increased up to 30 minutes. The optimal contact time to attain equilibrium was experimentally found to be 30 minutes. Beyond that, saturation of active sites was observed which do not allow further adsorption (Figure 4) [8].
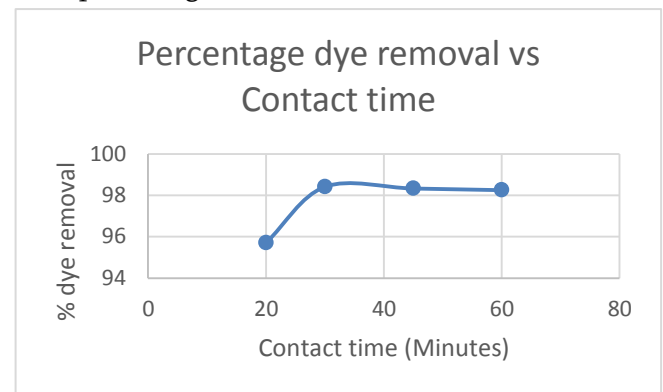

Figure 4. Effect of contact time

2) Effect of pH:

A range of 3.0 to 10.0 was selected for the optimization of pH and it was adjusted using 0.1 N HCl or 0.1N NaOH. The dye removal efficiency was found to be maximum at pH 7 (Fig 5) [14].
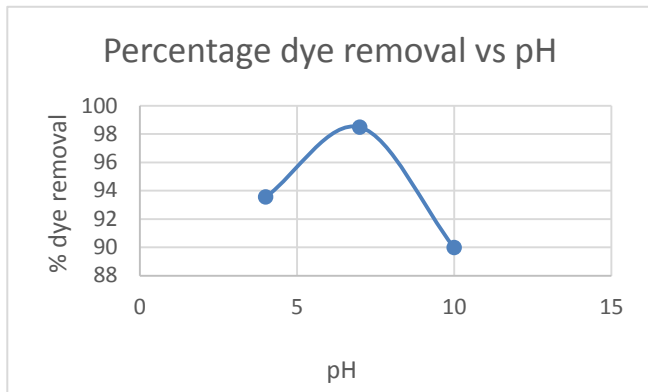
Percentage dye removal vs pH

Figure 5. Effect of pH

3) Effect of adsorbent dosage:

Adsorbent dose is the important parameter in the adsorption studies which determines the capacity of an adsorbent for a given initial concentration of the adsorbate [10]. To investigate the effect of mass of adsorbent on the adsorption of dye, a series of different adsorbent dosage ranging from 0.2 to 2.5g for 25mL was taken. An increase in the percentage removal efficiency up to 1.0g for 25mL of dye dosage is observed, beyond which it attains saturation/ shows less efficient removal of dye (Figure 6).
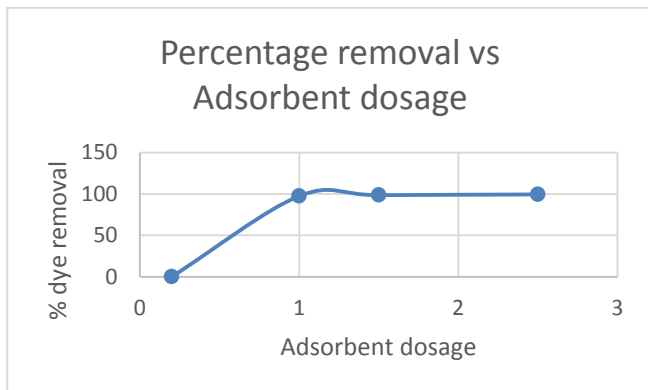
Percentage removal vs Adsorbent dosage

Figure 6. Effect of Adsorbent dosage

4) Effect of concentration of dye:

Concentrations ranging from 50 to 250 mgL^{-1} were selected and it was observed that with the increase in concentration, there is a decrease in the percent removal of the dye [15]. However, 100 mgL^{-1} was chosen as the optimized concentration of the dye for the further analysis as the amount of dye adsorbed on to the adsorbent

from the initial dye concentration was found to be maximum with the selected concentration (Fig 7).
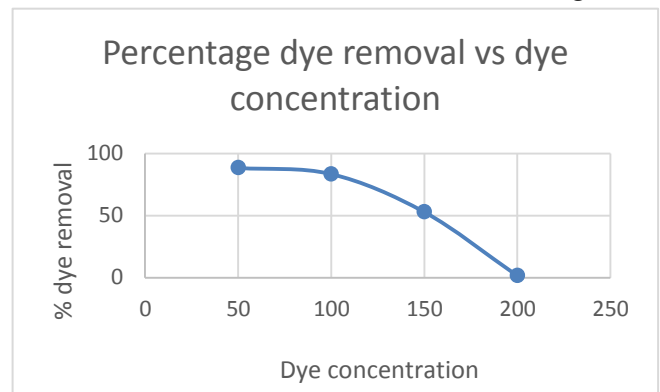
Percentage dye removal vs dye concentration

Figure 7. Effect of Dye concentration

5) Effect of temperature:

The temperature range of 25°C to 60^{0}C was investigated for all the samples. A very high temperature i.e beyond 45^{0}C was not found to be favourable for the adsorption process. This may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate with the temperature condition as mentioned above [8]. The ideal temperature of 45°C was selected for the further study (Figure 8).
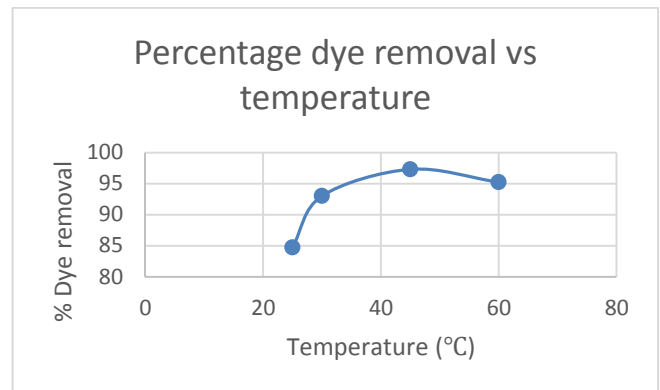
Percentage dye removal vs temperature

Figure 8. Effect of Temperature

G. Optimized Parameters:

Table 3. Optimized parameters

Sr.No	Parameters studied	Optimized Parameters
1	Contact time	30 minutes
2	pH	7
3	Adsorbent dosage	1g
4	Dye concentration	100mgL^{-1}
5	Temperature	45^{0}C

H. Possible use of adsorption property of fly ash for sustainable development:

The bulk utilization of fly ash in adsorption process is highlighted to achieve sustainable solution. The role of fly ash samples as good adsorbents, generated from the experimental data signifies the utility of these samples for a sustainable method development. Fly ashes, considered as major industrial waste materials, with its good adsorption properties could find enormous applications in reducing the issues specially in the areas of environmental pollution to a large extent. Apart from the known applications of fly ash, the current work has given a scope to identify the applications for the pre-treatment of samples having diverse nature which can further be analysed using techniques like HPTLC, HPLC etc. Samples can have many interfering agents which interfere in the analysis and hamper the performance of results. Most of the times activated charcoal is used for the removal of such interfering components but now-a-days focus has been shifted towards developing a low-cost adsorbent. The utilization of fly ash will create new revenues as well as business opportunities while protecting the environment.

IV. CONCLUSION

In the characterization study, the morphology of the samples indicates that the surface is rough and irregular which supports adsorption. BET surface area was observed in the range of SF1>WA>SF2>FOU>TPP. WA and SF1 showed comparatively high LOI value which could be the result of unburnt carbon present in the sample. Carbon helps in the adsorption process. XRF analysis depicts the presence of SiO_2 in all the samples as a major component which is a known adsorbent. SF1 showed comparatively high specific surface area, LOI and presence of SiO_2

which helps in the process of adsorption hence amongst all five samples SF1 showed maximum dye removal from aqueous solution after the optimization of all the parameters. Percentage dye removal from aqueous solution using SF1 was found to be 97.82%. Fly ash is a potent adsorbent which can be used for the treatment of samples having many interfering agents. Hence, such new technologies will extend and enhance the usefulness of fly ash as renewable resource for value added products and for ways of making industrial process more sustainable. There is a good scope of research to extend the applications of various fly ash as an effective adsorbent for sustainable development.

V. ACKNOWLEDGEMENT

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