A Review on the Utilization and Kinetics of Fly Ash

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Abstract—Fly ash, generated during the combustion of coal for energy production, is an industrial by-product which is recognized as an environmental pollutant. Because of the environmental problems presented by the fly ash, considerable research has been undertaken on the subject worldwide. In this paper, the utilization of fly ash in construction, as a low-cost adsorbent for the removal of various pollutants is discussed. A considerable amount of research has been conducted using fly ash for adsorption of NOx, SOx, organic compounds, dyes and other organic compounds in waters. It is found that fly ash is a promising adsorbent for the removal of various pollutants. The adsorption capacity of fly ash may be increased after chemical and physical activation. The adsorption kinetics of the removal of fluoride from water over lime stone slurry impregnated fly ash (LSFA) catalyst using batch mode has been investigated in the present study. BET surface area, XRF, XRD, FTIR and SEM techniques were used to characterize the physico-chemical of the catalyst. Adsorption data were modelled using the Freundlich and Langmuir adsorption isotherms and followed first order kinetic equation. Future research in these areas is also discussed.

Index Terms—Fly ash, Adsorption, Wastewater, Heavy metals, Dye, Organics, Zeolite, Construction

I. INTRODUCTION

Since wide scale coal firing for power generation began in the 1920s, many millions of tons of ash and related by-products have been generated. The current annual production of coal ash worldwide is estimated around 600 million tones, with fly ash constituting about 500 million tonnes at 75–80% of the total ash produced [1]. Thus, the amount of coal waste (fly ash), released by factories and thermal power plants has been increasing throughout the world, and the disposal of the large amount of fly ash has become a serious environmental problem. The present day utilization of ash on worldwide basis amounts to16% of the total ash [1].

Coal is a dominant commercial fuel in India. Fly ash can be considered as the world’s fifth largest raw material resource [2]. An estimated 25% of fly ash in India is used for cement production, construction of roads and brick manufacture [3]. Currently, the energy sector in India generates over 130 Mt of FA annually [4] and this amount will increase as annual coal consumption increases by 2.2%. The large scale storage of wet fly ash in ponds takes up much valuable agricultural land approximately (113 million m²), and may result in severe environmental degradation in the near future, which would be disastrous for India.

Fly ash particles are considered to be highly contaminating, due to their enrichment in potentially toxic trace elements which condense from the flue gas. Research on the potential applications of these wastes has environmental relevance, in addition to industrial interest. Most of the fly ash which is produced is disposed of as landfill, a practice which is under examination for environmental concerns. Disposal of fly ash will soon be too costly – if not forbidden. Considerable research is being conducted worldwide on the use of waste materials in order to avert an increasing toxic threat to the environment, or to streamline present waste disposal techniques by making them more affordable. It follows that an economically viable solution to this problem should include utilization of waste materials for new products rather than land disposal.

Fly ash is generally grey in color, abrasive, mostly alkaline, and refractory in nature. Fly ash also contains different essential elements, including both macronutrients P, K, Ca, Mg and micronutrients Zn, Fe, Cu, Mn, B, and Mo for plant growth. The geotechnical properties of fly ash (e.g., specific gravity, permeability, internal angular friction, and consolidation characteristics) make it suitable for use in construction of roads and embankments, structural fill etc. The pozzolanic properties of the ash, including its lime binding capacity makes it useful for the manufacture of cement, building materials concrete and concrete-admixed products. The chemical composition of fly ash like high percentage of silica (60–65%), alumina (25–30%), magnetite, Fe2O3 (6–15%) enables its use for the synthesis of zeolite, alum, and precipitated silica. The other important physicochemical characteristics of fly ash, such as bulk density, particle size, porosity, water holding capacity, and surface area makes it suitable for use as an adsorbent.

From the perspective of power generation, fly ash is a waste material, while from a coal utilization perspective, fly ash is a resource yet to be fully utilized; producers of thermal electricity are thus looking for ways to exploit fly ash. The
cement industry might use it as a raw material for the production of concrete. Coal fly ash discharged from power plants can also be utilized as a by-product, and its use in recycling materials for agriculture and engineering is also being studied [5,6]. The conversion of fly ash into zeolite has also been widely examined [7].

Another interesting possibility might be used as a low-cost adsorbent for gas and water treatment. Several investigations are reported in the literature on the utilization of fly ash for adsorption of individual pollutants in an aqueous solution or flue gas. The results are encouraging for the removal of heavy metals and organics from industrial wastewater. This paper will review the various applications of fly ash, including low-cost adsorbents for flue gas cleaning, wastewater treatment for removal of toxic ions and organic matters, synthesis of zeolite, mine backfill, light weight aggregate, road sub-base and construction/cement applications.

II. PROPERTIES OF COAL FLY ASH

Characterisation of fly ash in terms of composition, mineralogy, surface chemistry and reactivity is of fundamental importance in the development of various applications of fly ash.

Fly ash consists of fine, powdery particles predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature. The carbonaceous material in the fly ash is composed of angular particles. The particle size distribution of most bituminous coal fly ash is generally similar to that of silt (less than a 0.075 mm or No. 200 sieve). Although sub-bituminous coal fly ash is also silt-sized, it is generally slightly coarser than bituminous coal fly ash. The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area may vary from 170 to 1000 m²/kg [8–11]. The colour of fly ash can vary from gray to black, depending on the amount of unburned carbon in the ash. The chemical properties of fly ash are influenced to a great extent by the properties of the coal being burned and the techniques used for handling and storage.

The principal components of bituminous coal fly ash are silica, alumina, iron oxide, and calcium, with varying amounts of carbon, as measured by the loss on ignition (LOI). Lignite and sub-bituminous coal fly ash is characterized by higher concentrations of calcium and magnesium oxide and reduced percentages of silica and iron oxide, as well as lower carbon content, compared with bituminous coal fly ash. Very little anthracite coal is burned in utility boilers, so there are only small amounts of anthracite coal fly ash. According to the American Society for Testing Materials (ASTM C618) [12], the ash containing more than 70 wt% SiO₂+Al₂O₃, Fe₂O₃ and being low in lime are defined as class F, while those with a SiO₂, Al₂O₃, Fe₂O₃ content between 50 and 70 wt% and high in lime are defined as class C. The chief difference between Class F and Class C fly ash is in the amount of calcium and the silica, alumina, and iron content in the ash. In Class F fly ash, total calcium typically ranges from 1 to 12%, mostly in the form of calcium hydroxide, calcium sulphate, and glassy components, in combination with silica and alumina. In contrast, Class C fly ash may have reported calcium oxide contents as high as 30–40%. Another difference between Class F and Class C is that the amount of alkalis (combined sodium and potassium), and sulphates (SO₄), are generally higher in the Class C fly ash than in the Class F fly ash.

III. FLY ASH UTILIZATION

If you are using Word, use either the Microsoft Equation Editor or the MathType add-on (http://www.mathtype.com) for equations in your paper (Insert | Object | Create New | Microsoft Equation or MathType Equation). “Float over text” should not be selected.

A. Adsorbents for cleaning of flue gas

**Sulphur compounds**

Effort has been made to reduce SOx emissions by installing equipment for flue gas desulphurization (FGD). The wet type limestone scrubbing processes is widely used because of its high DeSOx efficiency and easy operation. However, these processes have drawbacks, such as high water consumption and the need for wastewater treatment [6]. In the Dry-type FGD large amount of absorbent is required as compared to wet-type FGD. This may be due to the fact that a higher molar ratio of calcium to sulphur is required to obtain a high DeSOx efficiency. The reactions are represented below.

\[
\begin{align*}
NO + \frac{1}{2} O_2 & \rightarrow NO_2 \\
SO_2 + NO & \rightarrow SO_3 + NO \\
Ca(OH)_2 + SO_3 & \rightarrow CaSO_4 + H_2O
\end{align*}
\]

As shown in the above chemical formulas, the sulfur dioxides in the flue gas are fixed as gypsum. On the other hand, they are fixed as sulfite in other conventional dry processes such as limestone injection and active manganese. Activated carbon was used to oxidize reduced sulphur compounds; however, it is too costly for large-scale environmental remediation applications. Coal fly ash is a cheap absorbent for dry-type FGD. Fly ash recycling in the flue gas desulphurization process has shown promising results.

The FGD process using coal ash has been commercialized, and during operation, there is no need for wastewater treatment or gas reheating, and so this process is considered to be an ideal choice for controlling the emission of sulfur dioxide and an environmentally friendly method for reuse of coal ash. Since the introduction of FGD in the late1960s, global market demand for FGD has been steady at between 5000 and 10,000 MW per year, and mainly wet-type limestone FGD units have been installed [13]. As described in this part, wet limestone FGD requires a wastewater treatment facility. Furthermore, it emits carbon dioxide (greenhouse gas) into the atmosphere as follows.

\[
CaCO_3 (Slurry) + SO_2 + \frac{1}{2} O_2 \rightarrow CaSO_4 (Slurry) + CO_2
\]

Dry-type FGD using fly ash is one of the processes that provide a solution to the above-mentioned problems, but this FGD has not yet spread worldwide.
B. Adsorption of NOx

Fly ash has also been proposed as adsorbents for NOx removal from flue gases [14]. The properties of fly ash particularly with respect to NOx adsorption – were closely examined for carbon content and specific surface area. It was found that unburned carbon remaining in the fly ash particle contribute the main surface area to fly ash, and the carbon can be activated to further improve the adsorption performance of the fly ash. Experimental results on activating coarser fly ash particles showed that adsorption capacity can be increased through controlled gasification of the unburned carbon. So, this carbon present in fly ash can be a precursor of activated carbons since it has gone through devolatilization during combustion in the power station furnace, and it, requires only a process of activation [15]. The adsorption of NOx using activated chars recovered from fly ash was reported [16]. Carbon-rich fractions from a gasifier were adsorbed one-third of the NOx compared with a commercial carbon. Recently, activated carbon from unburned carbon in coal fly ash has also been used for removal of NO[17].

C. Removal of toxic metals from wastewater

Fly ash has potential application in wastewater treatment because of its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its physical properties such as porosity, particle size distribution and surface area. Moreover, the alkaline nature of fly ash makes it a good neutralizing agent. Generally, in order to maximize metal adsorption by hydrous oxides, it is necessary to adjust the pH of wastewater using lime and sodium hydroxide [18,19].

Today, heavy metals are most serious pollutants, becoming a severe public health problem. Heavy metal and metalloid removal from aqueous solutions is commonly carried out by several processes such as, chemical precipitation, solvent extraction, ion exchange, reverse osmosis or adsorption etc. Among these processes, the adsorption process may be a simple and effective technique for the removal of heavy metals from wastewater.

D. Adsorption of various types of heavy metals on fly ash

Fly ash has been widely used as a low-cost adsorbent for the removal of heavy metal. Among the metal ions, Ni, Cr, Pb, As, Cu, Cd and Hg are the most often investigated. The use of fly ash for removal of heavy metals was reported as early as 1975. Gangolietal. [20] reported the utilization of fly ash for the removal heavy metals from industrial wastewaters.

E. Adsorption mechanism and kinetics

For a solid liquid adsorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intra particle diffusion or both. The adsorption dynamics can be described by the following three consecutive steps:

- transport of solute from bulk solution through liquid film to adsorbent exterior surface;
- solute diffusion into pore of adsorbent except for the small quantity of sorption on external surface;
- parallel to this is intra particle transport mechanism of surface diffusion;
- adsorption of solute on interior surfaces of the pores and capillary spaces of adsorbent.

The last step is an equilibrium reaction. Of the three steps, the third step is rapid and negligible. The overall rate of adsorption will be controlled by the slowest step that would be either film diffusion or pore diffusion controlled.

To review on the kinetics of the adsorption process an experiment was conducted by Shefali Saxena [21] and some good results came which is described as below.

IV. MATERIALS AND METHODS

A. Materials

Fly ash (Class F type) having SiO₂ (58%), Al₂O₃ (19%), Fe₂O₃ (8%), CaO (0.6%), MgO (0.6%), TiO₂ (1.3%), Na₂O (2.8%) and trace elements (4.1%) analyzed by X-ray fluorescence spectrometer was collected from Kota Super Thermal Power Station (Kota, Rajasthan, India). Lime stone slurry waste was procured directly from stone cutting industries at Kota. MgF₂ were pur chased from S.D. Fine Chem. Ltd., India and were used as such.

B. Catalyst Synthesis

The adsorption catalyst was synthesized by mixing fly ash and lime stone slurry in a fixed ratio of 3:1. The mixture was stirred continuously at 30 °C for 24 h. The mixture was then filtered and dried at 100 °C for 24 h to remove excess water. The dried material was milled in mortar for one hour for uniform sizing and increasing surface area. This material was finally calcined at 550 °C for 6 h.

C. Experimental Procedure

The stock solution of 100 mg/l fluoride was prepared by dissolving 5 g of anhydrous MgF₂ in 100 ml of distilled water. Fluoride removal studies were conducted using batch method. In which, a fixed amount of adsorbent LSFA (0.5 g), was added to 100 ml of fluoride solution of varying concentration (2, 6 and 10 mg/l) taken in stopped conical flasks, placed in a thermostated agitation (30 °C) assembly. The solution was agitated continuously (600 rpm) at constant temperature. The adsorbate uptake qe (mg/g), was calculated using eqn.(1) given by

\[ q_e = \frac{C_0 - C_e}{W} \times V \]

Where C₀ is the initial adsorbate concentration (mg/l); Cₑ is the equilibrium adsorbate concentration in solution (mg/l); V is the volume of the solution and W is the mass of the absorbent (g) and qₑ is the amount of absorbed fluoride. The kinetics was followed by withdrawing 0.5 dm-3 aliquot samples at different intervals. The absorbent was separated from aliquot by filtration through Whatman no. 42 filter paper. Residual concentration of fluoride ion was estimated using ion meter with fluoride ion selective electrode. Experimental runs were observed with initial rapid adsorption trends.
D. Catalyst characterization

The chemical components of the pure fly ash were analyzed by X-ray fluorescence Spectrometer (Philips PW1606). The BET surface area was measured by N2 adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using Quantachrome NOVA 1000e surface area analyzer. The FTIR (Fourier transform infrared) spectra of different samples were recorded using a Bruker FTIR spectrophotometer (Tensor-27) with DRS by mixing the sample with dried KBr (in 1/20 wt. ratio) in the range of 550-4000 cm-1 with a resolution of 4 cm-1. Powder X-ray diffraction studies were carried out by using (Philips X’pert) analytical diffractometer with monochromatic CuKα radiation (k = 1.54056 Å) in a 20 range of 0-80°. The morpho- logical and textural studies of the catalysts were performed by Scanning electron microscopy (Philips XL30 ESEM TMP).

V. RESULT AND DISCUSSION

The XRD and SEM results of the raw fly ash have been reported earlier in our literature data [22]. The XRD pattern of LSFA catalyst indicates the presence of calcium silicate (31°, 32°, 37°, 47°) and magnesium silicate (36°, 43°) phases [23, 24]. The SEM image of LSFA catalyst shows dense particles with distribution of varying particles size deposited lime stone slurry, with clearly visible on the external surface of fly ash particles. The specific surface areas of KTPS fly ash and LSFA catalyst are found to be 8 and 7 m²/g respectively.

Adsorption Isotherm Analysis

The analysis of adsorption data were accomplished with the help of the linear forms of Freundlich and Langmuir isotherms [25].

Freundlich isotherm

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  

Langmuir isotherms

\[ \frac{1}{q_e} = \left( \frac{1}{Q_m} \right) + \left( \frac{1}{Q_m} C_e \right) \]  

where \( q_e \) is the amount of adsorbed F- per unit weight of LSFA (mg/g), \( K_f \) and \( 1/n \) are Freundlich constant related to adsorption capacity and intensity respectively, \( C_e \) is the concentration of fluoride (mg/l) at equilibrium, \( Q_m \) is the maximum adsorption at monolayer coverage in mg/g, \( b \) is the Langmuir constant in mg/l.

The adsorption isotherms parameters along with the correlation coefficients for the various concentration of F- indicates a smaller value of 1/n at 10 mg/l of F-, which shows a better adsorption mechanism. The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor. The different types of isotherms can be described on the basis of r values which is as follows

\[ r \geq 1 \text{ unfavourable} \]
\[ r = 1 \text{ linear} \]
\[ r \leq 1 \text{ favourable} \]
\[ r = 0 \text{ irreversible} \]

The r values for the present experimental plots are in the range of 0.05 to 0.37, which favours the adsorption of MgF₂ on LSFA catalyst.

VI. ADSORPTION KINETIC STUDIES

The adsorption data were used at five different kinetic models using least square regression analysis for different initial concentration of fluoride. On the basis of high R² and low SEE, the most favorable model for fluoride adsorption kinetics is the first order at 2, 6 and 10 mg/l [F⁻], while two-rate constant and Elovich equation are completely rejected.

The values of slope, correlation coefficient (R²), and standard errors of estimate (SEE) at 10 mg/l [F⁻] indicates that the correlation coefficient value for the first order kinetic model (R²=0.9211) is higher than that obtained from the other kinetic models.

VII. FUTURE RESEARCH AND PROSPECTS

Fly ash has a great potential in environmental applications and interesting alternative to replace activated carbon or zeolites for adsorption in the air or water pollution treatment. Up to date, no industrial scale application has been realized. Economic barriers have to be overcome in terms of high value and high volume utilization for the industrial applications of fly ash.

Unburned carbon is an important component of fly ash, whose composition in fly ash varies with combustion efficiency. In fly ash, unburned carbon contents generally range between 2% and 12%. The higher percentage of unburned carbon in fly ash will lead to efficiency loss and poor marketability for cement production. Unburned carbon is similar to the precursors for production of premium carbon materials, such as, activated carbon. Activated carbon made from unburned carbon of fly ash has a significant potential of cost advantage over other activated carbon. Therefore, separation of unburned carbon from fly ash will be beneficial to fly ash application, either for carbon recycling or mineral fly ash application in cement production and zeolite synthesis. However, few investigations have been currently conducted in the utilization of unburned carbon for production of activated carbon. More efforts should be attempted in this area.

Fly ash can be considered as a valuable resource and needs to be studied, in order to facilitate the application of fly ash to new and innovative areas of economic interest. This review aimed to act as a stepping stone for the prospective researchers into the rewarding field of fly ash.

VIII. CONCLUSION

This paper has attempted to cover a wide spectrum of information so that the reader can better understand fly ash utilization. Understanding coal formation and combustion processes provides both a background and basis for the
alternative uses of the resultant fly ash. This review has shown that, in most cases, reported work to date in this area has been of laboratory scale, and further development work is needed.

Fly ash, although posing environmental pollution, it is an important raw material for various applications. The utilization of fly ash in construction, removal of organic compounds, heavy metals, dyes, and zeolite synthesis can help a great deal in the reduction of environmental pollution. For maximum benefit, new technologies for the efficient utilization of fly ash should be made use. To improve removal efficiencies and adsorption capacities, chemical modifications of fly ash is needed.

The LSFA catalyst examined in this study showed promising properties as a low-cost and effective adsorbent for the removal of fluoride from water. The adsorption kinetic data followed first order rate model and adsorption equilibrium data followed Freundlich and Langmuir isotherm model with a better fit. The impregnated lime stone slurry was not leached during the adsorption process.

The unburned carbon in fly ash plays an important role for adsorption and converted to activated carbon, which will enhance the adsorption capacity. Separation of unburned carbon from the minerals can bring benefits for applications of unburned carbon and utilization of mineral section for cement production and zeolite synthesis. There should be a greater emphasis on the development of new technology for efficient utilization of fly ash. Fly ash utilization programme must be extensively taken up covering various aspects at different level to minimize the environmental pollution. The review pointed out that the key issue of critical comparison between fly ash generated products and processes, and those derived from more ‘traditional’ routes has not been extensively tackled. More analysis of long-term economic and environmental impacts, possibly through employing life cycle assessments (LCAs) is needed. There is a scarcity of information on the environmental impact of fly ash as an ingredient in the preparation of materials.

REFERENCES