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Removal of Toxic Ions on Bio-adsorbent from Industrial Wastewater- A Review

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Abstract:

Dispersed writing is tackled to basically survey the conceivable source, science, potential biohazards and best accessible medicinal procedures for various lethal substantial metals Mercury, Cadmium and Iron generally found in wastewater. The ecological contamination is brought about by an assortment of toxins in water, air and soil. One of the major concerned poisons of living condition is "Dangerous Metals" likewise named as "Follow Elements". This term is utilized in geochemical and biochemical writing to allude to a gathering of in any case disconnected synthetic components which are found in nature at low focuses. Their fixations in various common habitats shift broadly. (Saroj Kumar et al. 2014). Since overwhelming metals are not wiped out from the sea-going biological system in nature process and hold there for longer time in this manner it is progressively hazardous for the humankind and condition. In ongoing past a variation of treatment procedures for the evacuation of various kind of contamination from water and wastewater have been grown, for example, organic strategies, physical techniques, synthetic strategies and incorporate techniques substance techniques comprise of decrease, precipitation, coagulation, particle trade and adsorption. Among all the strategies portrayed over the adsorption techniques is extraordinarily favoured as a development method for the treatment of water and wastewater because of its high productivity, simple taking care of and more affordable.

Keywords: Review Paper, Fly Ash, Toxic Metal, Removal of Metal ion, Thermodynamic studies.

1. INTRODUCTION

Water pollution is a major crisis around the world, where one- third of the pollution is caused by the industrial effluents discharge from chemical and Food industries after the industrial revolution, which increases the surface water pollution more than 20 times. Moreover, 20% of people died every year, due to the consumption of unsafe drinking water. Discharge of wastewater from textile industries, power plants, chemical industries contains the recalcitrant organic compounds and heavy metals1 which are toxic and non-bio gradable. Among various Industries, textile industries are noticeable, because they are consuming a large amount of water, energy, and chemical. Especially dyeing process in Textile industries use over 100,000 synthetic dyes in which 1-20% dyes are directly dispensed into the Textile wastewater, which causes 17-20% of water to get pollute. Generally, synthetic dyes preferred are azo dyes, VAT dyes, Indigoid, Cationic, phthalocyanine, Anthroquinone, Anionic, sulfur and Reactive dyes for dyeing and finishing processes. Comparing with other dyes Azo dyes are commercially viable which contains azo groups (N=N) with both the naphthalene and benzene rings.

Human health and Environmental related effects due to the presence of Benzidine in azo dyes are needed to be considered because of carcinogenic and mutagenic derivatives along the allergic reactions, skin degeneration, asthma, nausea, dysfunction of kidney, liver etc. Heavy metals present in wastewater such as mercury, Lead, Nickel, Cadmium etc., affects the agriculture products. In India, most of the fly ash is of class F type. Out of which 20-25% is being utilized in cement-based materials. In order to increase its percentage utilization, an investigation was carried out for its large scale utilization. Concrete mixtures were prepared by replacing cement with 40, 50, and 60% of fly ash. The concrete construction industry is not sustainable as it consumes huge quantities of important raw materials and the principal binder in concrete is Portland cement, the production of which is a major contributor to greenhouse gas that results in global warming and other climatic change. Many concrete structures suffer from lack of durability which has an adverse effect on the resource productivity of the industry.

Because the high-volume fly ash concrete system addresses all these sustainability issues, its use will enable the concrete construction industry to become more sustainable. Continuous research studies by various engineering research laboratories revealed its varied usefulness as an additive for enhancing the various qualities of concrete including its workability, strength and durability. Partial replacement of cement with fly ash in concrete save much of the energy required for production of OPC and also facilitates the economical disposal of millions of tons of fly ash. It has been found that in order to improve the other qualities of concrete like resistance of sulphate attack and thermal cracking, larger percentage of fly ash is to be used in concrete. The fly ash is less permeable to water, protecting reinforcing steel from corrosion and adding to the concrete‟s durability. It improves the workability of concrete because it aids in the placement of concrete into formwork and around reinforcing steel. Initially, the strength of high volume fly ash concrete is low but with the passage of time, it gains required strength. This can cause problems when slow strength gain means delays in construction. Fly ash admixtures can lengthen the time it takes for concrete to set. Sometimes this is desirable, particularly in hot weather which speeds up concrete set times, but at other times it is inconvenience and can cause delays in construction.

Adsorption mechanisms and interactions are needed to be considered to understand the kinetics of dye reduction. Physisorption, Ion-exchange, Precipitation and Chemisorptions are the main mechanisms associated with the interactions like Surface adsorption, Electrostatic interaction, and Vander Waals interaction, chelation, Proton displacement and covalent binding etc. Several isotherm models like Langmuir model, Elvis liquid film deposition model, Halsey model, Bruner-Emmet Teller model and etc., are present to define the contact between the pollutants adsorbed by the adsorbent and in water. The general characteristics possessed by the nano adsorbents should be of eco friendly basis, recyclable, excessive selectivity along adsorption capacity and ease of removal of dyes.

2. GENERAL PROPERTIES OF FLY ASH

Thermal power plants in India are primarily dependent on the combustion of bituminous coal. The low-lime fly ash similar to class F is the primary variety generated in India and significantly smaller volumes of high lime fly ash i.e. class C are also available. Indian low-lime fly ashes are characterized by a relatively higher concentration of SiO_2 and Al_2O_3 and lower contents of Fe_2O_3. The reactivity of fly ashes is dependent on their glass content and other mineral phases present. Indian fly ashes are more crystalline than those obtained in other countries, the glass content ranges from 47.0 to 60.9%. The properties of the Indian fly ashes are highly crystalline, relatively coarse and widely variable, the size of fly ash particles remains in the range of 3–9μm.

International fly ash consists of inorganic, incombustible matter present in the coal that has been fused during combustion into a glassy, amorphous structure. These fly ash particles are generally spherical in shape and range in size from 2μm to 10μm consists mostly of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3). Fly ash like soil contains trace concentrations of the following heavy metals nickel, vanadium, cadmium, barium, chromium, copper, molybdenum, zinc and lead. The particle sizes in fly ash vary from <1 μm up to more than 100 μm with the typical particle size measuring under 20 μm.

Table 1

Generation and utilization of fly-ash in different countries

Country	Fly-Ash Production (million Tons/year)	Fly-Ash Utilization
India	112	38
China	100	45
USA	75	65
Germany	40	85
UK	15	50
Australia	10	85

Fly-ash is the end residue from combustion of pulverized bituminous or sub-bituminous coal (lignite) in the furnace of thermal power plants and consists of mineral constituents of coal which is not fully burnt. Fine minute particles of ash are carried away with flue gases in electrostatic precipitators or cyclone separators and are collected by wet (slurry form) or dry scrubbing method, which requires large volumes of land, water and energy. Use of high ash containing (30–50%) bituminous or sub-bituminous coal in thermal power stations, in addition to several captive power plants, contributes to indiscriminate disposal of this industrial waste every year . The coal ash by-product has been classified as a Green List waste under the Organization for Economic Cooperation and Development (OECD). It is not considered as a waste under Basel Convention. However, in many countries this industrial by-product has not been properly utilized rather it has been neglected like a waste substance. In China, about 100 MT (million tons) of coal combustion products are produced each year. In India, presently, the figure is around 112 MT and is likely to exceed 170 MT by 2012 [4]. During 2005, the utilization of fly-ash was 100% in Italy, Denmark and Netherlands with an annual production of 2 MT, 50–85% in USA and Germany and 45% in China (Table 1). In India, fly-ash utilization has increased from 3% in the 1990s to 38%. The reason of low fly-ash utilization in India is the unavailability of appropriate cost-effective technologies. According to the report of American Coal Ash Association, in agriculture, wasteland reclamation and civil engineering purposes use 32% of the fly-ash, 30% of the bottom ash, 94% of the boiler slag and 9% of flue gas desulfurization sludge.

Many experiments and studies on the effect and potentiality of fly-ash as an amendment in agricultural applications have been conducted by various agencies, research institutes at dispersed locations all over the world. In this paper, utilization of fly-ash as a value-added product of agriculture is reviewed with the aim of helping opening up the usage of fly-ash and reducing the environmental and economic impacts of disposal.

3. PHYSICAL PROPERTIES OF FLY-ASH

The physical properties of fly-ash vary widely depending on the coal type, boiler type, ash content in coal, combustion method and collector setup. Fly-ash generally has a silt loam texture with 65–90% of the particles having a diameter of less than 0.010 mm. Ash from bituminous coal is usually finer as compared with that of lignite one. Fly-ash particles are empty spheres (cenospheres) filled with smaller amorphous particles and crystals (plerospheres). The cenosphere fraction constitutes as much as 1% of the total mass and gets easily airborne. In general, fly-ash has low bulk density (1.01–1.43 g cm^{-3}), hydraulic conductivity and specific gravity (1.6–3.1 g cm^{-3}). Mean particle densities for non- magnetic and magnetic particles are 2.7 and 3.4 g cm^{-3}, respectively, while the moisture retention ranges from 6.1% at 15 bar to 13.4% at 1/3 bar. By virtue of its physical characteristics and sheer volumes generated, fly-ash is a serious problem. Some of the aspects of the problem are:

(1) Due to heavy disposal, fly-ash particles both as dry ash and pond ash occupy many hectares of land in the vicinity of power station.

(2) Because of its fineness, it is very difficult to handle fly-ash in dry state. Flying fine particles of ash corrode structural surfaces and affect horticulture

(3) It disturbs the ecology through soil, air and water pollution.

(4) Long inhalation of fly-ash causes various serious diseases like silicosis, fibrosis of lungs, bronchitis, and pneumonitis. Moreover, the oxides of iron and aluminium present on the surface of the fly-ash particles attract toxic trace elements, such as Sb, As, Be, Cd, Pb, Hg, Se, and V, and they are found to be concentrated largely on the surface of fly-ash ..

4. CHEMICAL PROPERTIES OF FLY-ASH

The factors influencing the physical properties are also responsible for wide variation of chemical properties of fly-ash. In a study of 11 fly-ashes from various U.S. power plants The major components were Al, Fe and Si, with smaller concentrations of Ca, K, Na, Ti, and S. Fly-ash contains varying amounts of numerous trace elements, some of which are required by plant and animals in varying amounts, whereas some may have toxic effect.

Fly-ash contains essential macronutrients including P, K, Ca, Mg and S and micronutrients like Fe, Mn, Zn, Cu, Co, B and Mo. Some are rich in heavy metals such as Cd and Ni.(Kumar et al) on an average 95–99% of fly-ash consists of oxides of Si, Al, Fe and Ca and about 0.5–3.5% consists of Na, P, K and S and the remainder of the ash is composed of trace elements. It is considerably rich in trace elements like lanthanum, terbium, mercury, cobalt and chromium (Page et al.) many trace elements including As, B, Ca, Mo, S, Se and Sr in fly-ash are concentrated in the smaller ash particles. In fact, fly-ash consists of practically all the elements present in soil except organic carbon and nitrogen. On the basis of silica, alumina and iron oxide content, fly-ash has been classified into two types: Class F (low lime) and Class C (high lime) (ASTM C618). The chemical properties of the fly-ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite). Anthracite is a hard, compact variety of mineral coals that has a high lustre. It has the highest carbon count and contains the fewest impurities of all coals, despite its lower calorific content. Lignite, also referred to as brown coal, is the lowest rank of coal and used almost exclusively as fuel for steam-electric power generation. The burning of harder, older anthracite and bituminous coal typically produces Class F fly-ash. Fly- ash produced from the burning of younger lignite or sub-bituminous coal is of Class C. Alkali and sulfate (SO_4) contents are generally higher in Class C than Class F fly-ash. Lignite or brown coal is used almost exclusively as fuel for steam- electric power generation, resulting in the production of huge amount of fly-ash. Therefore, use of brown fly-ash in agriculture deserves special attention.

Al in fly-ash is mostly bound in insoluble aluminosilicate structures, which greatly confines its biological toxicity. Fly- ash also contains minerals such as quartz, mullite, hematite, magnetite, calcite and borax, and oxidation of C and N during combustion drastically reduces their quantity in ash. Depending on the sulfur content of the parent coal, the pH of fly-ash varies from 4.5 to 12.0 and the type of coal used for combustion affects the S content of fly-ash. Generally high S and produces acidic ash, while western US lignite coals are lower in S and higher in Ca and thereby produce alkaline ash. The coal in India contains low S but high ash (40%).

Table 2

Physical characteristics and the major & trace elements in electrostatic precipitator (ESP) fly-ash and soil

PROPERTIES	**FLY-ASH**	**SOIL**
Bulk density (g cc^{-1})	<1.0	1.33
Water-holding capacity (%)	35–40	<20
Porosity (%)	50–60	<25
Major elements in percentages		
N	–	0.01–1.0
P	0.004–0.8	0.005–0.2
K	0.15–3.5	0.04–3.0
Ca	0.11–22.2	0.7–50
Mg	0.04–7.6	0.06–0.6

S	0.1–1.5	0.01–2.0
Al	0.1–17.3	4–30
Na	0.01–2.03	0.04–3.0
Fe	36–1333	0.7–55
Trace elements in mg kg^{-1}		
Mn	58–3000	100–4000
Zn	10–3500	10–300
Cu	14–2800	2–100
B	10–618	2–100
As	2.3–6300	0.1–40
Cd	0.7–130	0.01–7.0
Co	7–520	1–40
Cr	10–1000	5–3000
Hg	0.02–1.0	–
Mo	7–160	0.2–5.0
Ni	6.3–4300	10–1000
Pb	3.1–5000	2–100
Se	0.2–134	0.1–2.0

A large portion of inorganic compounds vaporizes in the cooler parts of the installation during the combustion of ground coal at a high temperature of 400–1500 °C and condenses on fly-ash particles. Three groups of elements were recognized on the basis of this volatilization–condensation hypothesis which established correlation between mineral concentrations with the particle size. These groups are: group I with pronounced concentration of As, Cd, Ni, Pb, S, Sb, Se, Ti and Zn; group II with limited concentration of Be, C, Fe, Mg, Mn, Si and V and group III with no concentration of Ca, Co, Bi, Cu, Sn and Ti. Group I elements are classified as „litho files" (Al, Ca, Fe, K, Mg, Na, Ti) with little or no enrichment in smaller fly-ash particles, group II elements as „Chalco files" (As, Cd, Mu, Pb, Sb, Se) with increased concentration with decreasing particle size and group III elements (Be, Cu, Ni, V, Co) have intermediate behavior and are enriched in smaller particles but to a lesser extent than those of group II. The properties and contents of major and trace elements of soil and fly-ash that are available in the literature are presented in Table 2.

5. FLY-ASH FOR IMPROVING SOIL PROPERTIES

Soil properties as influenced by fly-ash application have been studied by several workers for utilizing this industrial waste as an agronomic amendment. Physical and chemical properties of soil due to fly-ash amendment vary according to the original properties of soil and fly-ash but certain generalization could be made in most cases

Soil texture

Alteration of the soil texture is possible through the addition of appropriate quantities of fly-ash (Several experiments have been performed to measure the physical properties for a variety of soils mixed with up to 50% fly-ash, which revealed that soil fly-ash mixture tend to have lower bulk density, higher water-holding capacity and lower hydraulic conductivity than soil alone) due to its textural manipulation through fly-ash mixing.

Application of high rates of fly-ash can change the surface texture of soils, usually by increasing the silt content. Fly-ash addition at 70 t ha^{-1} has been reported to alter the texture of sandy and clayey soil to loamy. Addition of fly-ash at 200 t $acre^{-1}$ improved the physical and chemical properties of soil and shifted the USDA textural class of the refuge from sandy loam to silt loam .

Bulk density

The particle size range of fly-ash is similar to silt and changes the bulk density of soil. (Several experiments have been performed to measure the physical properties for a variety of soils mixed with up to 50% fly-ash , which reveals that soil fly-ash mixture tend to have lower bulk density, higher water-holding capacity and lower hydraulic conductivity than soil alone.) Chang et al. observed that among five soil types, Reyes silty clay showed an increase in bulk density from

0.89 to 1.01 g cc^{-1} and a marked decrease in soils having bulk density varying between 1.25 and 1.60 g cc^{-1} when the corresponding rates of fly-ash amendment increased from 0% to 100%. Application of fly-ash at 0%, 5%, 10% and 15% by weight in clay soil significantly reduced the bulk density and improved the soil structure, which in turn improves porosity, workability, root penetration and moisture-retention capacity of the soil addition of fly-ash up to 46% reduced the dry density of the soil in the order of 15–20% due to the low specific gravity and unit weight of soil.

Water-holding capacity

Fly-ash application to sandy soil could permanently alter soil texture, increase micro porosity and improve the water- holding capacity as it is mainly comprised of silt-sized particles. Fly-ash generally decreased the bulk density of soils leading to improved soil porosity, workability and enhanced water-retention capacity. A gradual increase in fly-ash concentration in the normal field soil (0, 10, 20up to 100% v/v) was reported to increase the porosity, water-holding capacity, conductivity and cation-exchange capacity. This improvement in water-holding capacity is beneficial for the growth of plants especially under rain fed agriculture. Amendment with fly-ash up to 40% also increased soil porosity from 43% to 53% and water-holding capacity from 39% to 55%. Fly-ash had been shown to increase the amount of plant available water in sandy soils.

Chang et al. found that fly-ash amendment increased the water-holding capacity of sandy/loamy soils by 8%, which in turn caused improvement in hydraulic conductivity and thereby helped in reducing surface encrustation. Water-holding capacities of fly-ashes from different thermal power plants in Eastern India were compared, and the effect of size fractionation on the water-holding capacity was determined in an investigation by Sarkar and Rano. Results revealed that the fly-ash obtained from a thermal power plant working on stoker-fired combustor produced the highest water-holding capacity, followed by the one working on pulverized fuel combustor. Fly-ash collected from super thermal power plant had the least water-holding capacity (40.7%). The coarser size fractions of fly-ashes in general comprised higher water-holding capacity than the finer ones. According to Jala and Goyal, the Ca in fly-ash readily replaces Na at clay exchange sites and thereby enhances flocculation of soil clay particles, keeps the soils friable, enhances water penetration and allows roots to penetrate compact soil layers.

Soil pH

Depending on the source, fly-ash can be acidic or alkaline, which could be useful to buffer the soil pH. The hydroxide and carbonate salts give fly-ash one of its principal beneficial chemical characteristics, the ability to neutralize acidity in soils. Fly-ash has been shown to act as a liming material to neutralize soil acidity and provide plant-available nutrients. Most of the fly-ash produced in India is alkaline in nature; hence, its application to agricultural soils could increase the soil pH and thereby neutralize acidic soils. Researchers have shown that the use of fly-ash as liming agent in acid soils may improve soil properties and increase crop yield. The concentration of easily soluble Ca (24.5 g kg^{-1} (dry weight)) in the fly-ash from a fluidized bed boiler at the industrial power plant of Laanilan Voima Oy in Oulu, Northern Finland was 15 times higher than the typical value of 1.6 g kg^{-1} (dry weight) in arable land in Central Finland. It is indicative of the fact that fly-ash is a potential agent for soil remediation and soil fertility improvement. The use of excessive quantity of fly-ash to alter pH can increase the soil salinity especially with unweathered fly-ash. An appreciable change in the soil physicochemical properties, an increase in pH and increased rice crop yield were obtained by mixed application of fly-ash, paper factory sludge and farmyard manure.

Biological properties

Information regarding the effect of fly-ash amendment on soil biological properties is very scanty. The results of several laboratory experiments revealed that application of unweathered fly-ash particularly to sandy soil greatly inhibited the microbial respiration, enzymatic activity and soil N cycling processes like nitrification and N mineralization. These adverse effects were partly due to the presence of excessive levels of soluble salts and trace elements in unweathered fly-ash. However, the concentration of soluble salts and other trace elements was found to decrease due to weathering of fly-ash during natural leaching, thereby reducing the detrimental effects over time. Moreover, the use of extremely alkaline (pH 11–12) fly-ash could also be the reason for those adverse effects. The application of lignite fly-ash reduced the growth of seven soilborne pathogenic microorganisms as reported by Karpagavalli and Ramabadran, whereas the population of *Rhizobium* sp. and P-solubilizing bacteria were increased under the soil amended with either farmyard manure or fly-ash individually or in combination. Gaind and Gaur found that the application of fly-ash at 40 t ha^{-1} in conjunction with *Pseudomonas striata* inoculation improved the bean yield, nutrient uptake by grain and highest population of the bacteria in the inoculated series, though both 40 and 60 t ha^{-1} of fly-ash along with *P. striata* resulted in the same amount of available P_2O_5 in the soil The soil fly-ash environment was the most suitable for the proliferation of these bacteria, thereby contributing towards enhanced availability of soil phosphorus [68]. Amendment of Class F, bituminous fly-ash to soil at a rate of 505 Mg ha^{-1} did not cause any negative effect on soil microbial communities and improved the populations of fungi, including arbuscular mycorrhizal fungi and gram-negative bacteria as revealed from analysis of community fatty acids. A pot-culture experiment was conducted by Garampalli et al. using sterile, phosphorus-deficient soil to study the effect of fly-ash at three different concentrations viz., 10 g, 20 g and 30 g fly- ash kg^{-1} soil on the infectivity and effectiveness of Vescicular-arbusculer mycorrhiza (VAM) *Glomus aggregatum* in pigeonpea (*Cajanus cajan* (L.) Millsp.) cv. Maruti. All the three different concentrations of fly-ash amendment in soil were found to significantly affect the intensity of VAM colonization inside the plant roots and at higher concentration (30 g fly-ash kg^{-1} soil); the formation of VAM fungal structure was suppressed completely. The dry weight of the pigeonpea plants under the influence of fly-ash amendment in VAM fungus-infested soils was found to be considerably less (though not significant enough) when compared to the plants grown without fly-ash that otherwise resulted in significant increase in growth over the plants without *G. aggregatum* inoculation.

However, fly-ash amendment without VAM inoculation was also found to enhance the growth of plants as compared to control plants (without fly-ash and VAM inoculum). The isolated 11 bacterial strains from the rhizospheric zone of *Typha latifolia* and inoculated separately in the fly-ash with additional source of carbon to investigate their ability to increase the bioavailability or immobilization of toxic metals like Cu, Zn, Pb, Cd and Mn. It was found that most of the bacterial strains either enhanced the mobility of Zn, Fe and Mn or immobilized Cu and Cd with the exceptions that NBRFT6 enhanced immobility of Zn and Fe and NBRFT2 of Mn. The study also revealed that NBRFT8 and NBRFT9 enhanced bioavailability of Cu and all the strains immobilized Cd. They explained that it was the specific function of bacterial strains, which caused the mobility/immobility of trace metals from the exchangeable fractions depending upon the several edaphic and environmental factors. Therefore, based on the extractability of metals from fly-ash, bacterial strains can be utilized to enhance the phytoextraction of metals from fly-ash by metal-accumulating plants or for arresting their leaching to water bodies.

6. FLY-ASH AS A SOURCE OF PLANT NUTRIENTS

To solve the soil-shortage problem in subsided land of coal mines, the principal chemical properties of artificial soil comprising organic furfural residue and inorganic fly-ash were examined The results indicated that the artificial soil was suitable for agricultural use after irrigation and desalination. The available nutrients in the artificial soil could satisfy the growth demand of plants, and the pH tended to neutrality. Chemically, fly-ash contains elements like Ca, Fe, Mg, and K, essential to plant growth, but also other elements such as B, Se, and Mo, and metals that can be toxic to the plants. Lime in fly-ash readily reacts with acidic components in soil leading to release of nutrients such as S, B and Mo in the form and amount favourable to crop plants. Fly-ash contains negligible amount of soluble salt and organic carbon and adequate quantity of K, CaO, MgO, Zn and Mo. However, it is potentially toxic to plants due to high B content (345 mg kg^{-1}) . After application of fly-ash, the downward move of nutrients through soil column and the availability of nutrients for plant growth became limited to a depth of 80 cm from the soil surfacea gradual increase in fly-ash concentration in the normal field soil from 0, 10, 20 up to 100% v/v increased the pH, thereby improving the availability of sulfate, carbonate, bicarbonate, chloride, P, K, Ca, Mg, Mn, Cu, Zn and B. They also found that addition of fly-ash to acidic and alkaline soil decreased the amounts of Fe, Mn, Ni, Co and Pb released from acid soil. However, the release of these metals from alkaline soil remained unchanged. The changes in the selected properties and heavy metal contents of three soil types in India were studied. The mixtures of soil with different proportion of fly-ash and sludge, either alone or in combination, at a maximum application rate of 52 t ha^{-1} were incubated for 90 day at near field capacity moisture level. Sewage sludge, due to its acidic and saline nature, high organic matter and heavy metal contents, had more impact on soil properties than the fly-ash. Electrostatic precipitator (ESP) ash collected directly from thermal power station in Bathinda, India, was more fine-textured, lower in pH and richer in nutrients than the ash of dumping sites [30]. The ashes had both higher saturation moisture percentage and lower bulk density as compared to the normal cultivated soils. The dominant cation on the exchange complex was found to be Ca^{2+} followed by Mg^{2+}, Na^{+} and K^{+} in addition to high S content. In a study with methi (*Trigonella foenum–graecum*), applied different basal doses of fly-ash at 0, 5, 10 and 15 t ha^{-1} along with two doses of nitrogen (40 and 20 kg ha^{-1}). Uniform basal dose of 30 kg P and 40 kg K ha^{-1} was also applied. In general, fly-ash at 10 t ha^{-1} with 20 kg N ha^{-1} proved better, while higher dose of fly-ash proved deleterious. Fly-ash is not recognized as an optimal source of phosphorus as it was found inferior to monocalcium phosphate. However, it hastened Ca^{2+} and Mg^{2+} uptake by legumes.

7. USE OF FLY-ASH IN COMPOSTING

In sewage sludge composting, lime is used to raise the pH and thereby to kill pathogens and to reduce the availability of heavy metals enriched in sludge. Since alkaline coal fly-ash contain a large amount of CaO, it can serve the purpose of lime, as it reduced the availability of heavy metals by physical adsorption and precipitation at high pH. Moreover, it is also cheaper than lime. Co-composting of fly-ash at 20% level with wheat straw and 2% rock phosphate (w/w) for 90 day recorded lowest C, N of 16.4:1 and highest available and total phosphorus [82]. Mixing alkaline fly-ash with highly carbonaceous acidic material to make compost for soil treatment had also been suggested. The low nitrogen content of fly-ash is an important constraint for its agricultural application.

A study the possibility of improving N status in mixtures of fly-ash and organic matter by implementing vermicomposting technology different combinations of fly-ash and cow dung viz., fly-ash alone, cow dung alone and fly-ash + cow dung at 1:1, 1:3 and 3:1 ratios were incubated with and without epigeic earthworms (*Eisenia foetida*) for 50 day. Results revealed that different bio-available forms of N, such as easily mineralizable NH^{4+} and NO_{3-}, considerably increased in the series treated with earthworms. It could be largely attributed to augmented microbiological activity in the vermicomposted samples and also to considerable rise in the concentration of N-fixing bacteria in this series. Among the three combinations, the highest availability of N was recorded in 1:1 mixture of vermicomposted fly- ash and cow dung. For proper fly-ash/sludge ratios, the fly-ash could also act as an outstanding neutralizer in the acidic waste. Leaching of heavy metals from the aggregate samples was below the environmental limits within a pH range between 3 and 9.

8. EFFECT OF FLY-ASH ON UPTAKE OF NUTRIENTS AND TOXIC ELEMENTS AND QUALITY OF CROP YIELD

The high concentration of elements like K, Na, Zn, Ca, Mg and Fe in fly-ash increases the yield of agricultural crops. However, application of unweathered fly-ash may have a tendency of accumulating elements such as B, Mo, Se and Al, which at toxic levels are responsible for reductions in the crop yields and consequently influence animal and human health. Fly-ash application might also decrease the uptake of heavy metals including Cd, Cu, Cr, Fe, Mn and Zn in plant tissues which could be probably due to the increased pH of fly-ash-amended soil the supply from fly-ash to plants might be short-term. Integrated nutrient treatments involving fly-ash at 10 t ha^{-1}, organic wastes and chemical fertilizers resulted in higher uptake of N, P, K, Ca, Mg, Fe, Mn, Zn and Cu in rice grain than application of only chemical fertilizers, which in turn was responsible for higher rice yield. They also observed lower concentration of Cd and Ni in both grain and straw of rice and the reason might be the increase in soil pH due to the application of fly-ash to the rice crop which precipitated the native Cd and Ni. In rice-based cropping system, uptake of N, P, K, Ca, Mg, S, Fe, Mn, Zn and Cu by subsequent mustard crop was higher under the residual fertility of fly-ash at 10 t ha^{-1} + paddy straw at 5 t ha^{-1} + chemical fertilizers or fly-ash at 10 t ha^{-1} + farmyard manure at 5 t ha^{-1} + chemical fertilizers or fly-ash at 10 t ha^{-1} + green manure at 2.5 t ha^{-1} + chemical fertilizers as compared to chemical fertilizers or fly-ash alone

9. EFFECT OF FLY-ASH ON GROUND WATER

Physical and chemical characteristics of fly-ash and hydro geologic and climatic conditions of the disposal site are the main factors, which determine the influence of ash on ground water. Weathered fly-ash contains higher level of soluble salt; therefore, deposition of this ash causes more ground–water contamination. In case of unweathered ash, there is generally a higher release of soluble salts initially, but it declines rapidly with time. When water saturated, weathered ash from a settling pond is deposited in a landfill, there is a rapid release of leachate containing much lower concentration of soluble salts, while it may take a year or longer for dry unweathered ash to absorb sufficient moisture to release lactates.

Fly-ash contains trace and heavy metals, which readily percolate down from conventionally used earth-lined lagoons. The solubility of trace and heavy metals present in fly-ash is <10% . Laboratory experiments revealed that 5–30% of toxic elements especially Cd, Cu and Pb are leachable. Moreover, the concentration of these elements in fly-ash is very low; hence, the chance for leaching of these elements to ground water is negligible. However, close monitoring of this aspect may be advisable. Experiments conducted at Central Fuel Research Institute (CFRI), Dhanbad, India showed that there was no negative influence of fly-ash application on the quality of ground water and that the trace and toxic metal contents were within the permissible limits. The potential use of fly-ash from coal-fired power plant for the removal of Zn(II) and Ni(II) from aqueous solutions has been reported. A study conducted on soils from Italian mine site contaminated severely with heavy metals showed decreased levels of heavy metal content in percolating water when mixed with fly-ash, which was indicative of the fact that fly-ash in such soils can lead to immobilization of heavy metal ions .

10. FLY-ASH UTILIZATION AND GLOBAL WARMING

Agriculture plays a major role in the global fluxes of the greenhouse gases like carbon dioxide, nitrous oxide, and methane. Many studies suggested that additional opportunities have arisen for lessening the GWP (global warming potential) by altering the agronomic practices. With the assumption by the Intergovernmental Panel on Climate Change (IPCC) that all the carbon in agricultural lime (aglime) is eventually released as CO_2 to the atmosphere, the US EPA estimated that 9 Tg (Teragram = 10^{12} g = 10^6 metric tonne) CO_2 was emitted from an approximate 20 Tg of applied aglime As per another estimate, in US agriculture only, aglime is applied to the tune of 20–30 Tg year^{-1} and the same study estimated that 4.4–6.6 Tg CO_2 was emitted in 2001 from that lime estimated the net CO_2 fluxes from liming of agricultural soils in Brazil for the period 1990–2000. The calculation was based on the methodology proposed by the IPCC, but separately conducted for the five administrative Brazilian regions. The summarized annual CO_2 emission for Brazil varied from 4.9 to 9.4 Tg CO_2 year^{-1} with a mean CO_2 emission of about 7.2 Tg CO_2 year^{-1}. But agricultural lime can be a source or a sink for CO_2, depending on whether reaction occurs with strong acids or carbonic acids. A study showed that infiltrating waters tended to indicate net CO_2 uptake, as did tile drainage waters and streams draining agricultural watersheds. As nitrate concentrations increased in infiltrating waters, lime switched from a net CO_2 sink to a source, implying nitrification as a major acidifying process . One experimental study demonstrated that 1 ton of fly-ash could sequester up to 26 kg of CO_2, i.e., 38.18 ton of fly-ash per ton of CO_2 sequestered. This confirmed the possibility to use this alkaline residue for CO_2 mitigation Use of fly-ash as soil ameliorant in place of lime could lead to reduction in CO_2 emissions, thus contributing to minimize global warming.

11. CONCLUSIONS

To meet the growing energy demand and thereby increase power generating capacity, the dependency on coal for power generation and disposal of fly-ash will continue to increase along with various unavoidable problems. Moreover, keeping in view of developmental problems like burgeoning population, growing food demand, shrinking natural resources, it is necessary to sustain the production of crop yield as well as soil health in an eco-friendly way. Hence, it is required to involve fly-ash more effectively in agriculture sector to exploit its various physical and chemical properties fully, which are beneficial for soil and crop health

Indian fly ash are mostly of class F which is a low lime fly ash characterized by a relatively higher concentration of SiO_2 and Al_2O_3 and lower contents of Fe_2O_3 whereas international fly ash are mostly of class C which is a high lime fly ash, generally spherical in shape and range in size from 2μm to 10μm consist mostly of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3) high volume of fly ash in the concrete result in the reduction of drying shrinkage in the concrete. High volume fly ash concrete (up to 40% cement replacement) showed better abrasion resistant particularly at high compressive strength. The compressive strength of high volume fly ash concrete is low at initial ages but with the passage of time i.e. beyond 28 days, it gains better compressive strength as compare to normal concrete. High volume fly ash concrete achieves satisfactory tensile strength as compare to normal concrete with the passage of time. However, the flexural strength of all mixes decreases as the percent replacement of fly ash increases.

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