Abatement of organic pollutants using fly ash based adsorbents

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ABSTRACT

The presence of organic pollutants in the environment is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment. It is a well-known fact that, these pollutants can damage nerves, liver, and bones and could also block functional groups of essential enzymes. Conventional methods for removing dissolved pollutants include chemical precipitation, chemical oxidation or reduction, filtration, ion-exchange, electrochemical treatment, application of membrane technology, evaporation recovery and biological treatment. Although all the pollutant treatment techniques can be employed, they have their inherent advantages and limitations. Among all these methods, adsorption process is considered better than other methods because of convenience, easy operation and simplicity of design. A fundamentally important characteristic of good adsorbents is their high porosity and consequent larger surface area with more specific adsorption sites. This paper presents a review of adsorption of different pollutants using activated carbon prepared from fly ash sources and the attendant environmental implications. Also, the ways of overcoming barriers to fly ash utilization together with regeneration studies are also discussed.

Key words | adsorption, contaminants, environment, fly ash

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INTRODUCTION

Globally, water is one of the most vital human resources that has economic, social, political and environmental importance throughout the world (Aguilera-Klink *et al.* 2000; Savenije 2002). Water pollution has become a serious environmental problem and has attracted global concern in recent years, particularly since various pollutants are entering aquatic systems as a result of rapid industrialization and urbanization (Bhatnagar & Sillanpää 2010). Contaminants that are of primary concern include metals, dyes, biodegradable waste, phosphates and nitrates, heat, sediment, fluoride, hazardous and toxic chemicals, radioactive pollutants, pharmaceuticals and personal care products (Namasivayam & Kavitha 2003; Bhatnagar & Sillanpää 2011; Bhatnagar *et al.* 2011; Adegoke & Bello 2015).

Trace amounts of any of these compounds lead to an enormous pollution problem and, consequently, the treatment of wastewater is a subject of paramount importance. Researchers in the analytical, environmental and material sciences have attempted to develop processes for removing various pollutants and currently, adsorption has become a widely used technology for the removal of both inorganic and organic material (Ali & Gupta 2007; Ali 2012). A number of materials have been investigated extensively for this purpose (Reddy *et al.* 2010, 2012) and activated carbon has undoubtedly been the most popular and efficient adsorbent used widely throughout the world for the removal of different pollutants (Rivera-Utrilla *et al.* 2011; Mezohegyi *et al.* 2012). However, activated carbon is relatively expensive, and this has restricted its application at times, thus making the alternative cost-effective adsorbents preferred for the treatment of pollutant-contaminated waste streams and aqueous systems (Bello *et al.* 2013). The valorization of agricultural wastes into valuable materials without generating pollutants is a major challenge and recommended for an industrial sustainable development in order to preserve the environment (Reddy *et al.* 2010).

Fly ash is one of solid wastes largely produced from power generation as coal combustion residue has a great potential in environmental applications and an interesting alternative to replace activated carbon or zeolites as an

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adsorbent for the treatment of wastewater (Wang *et al.* 2005a, 2005b). The technical feasibility of utilization of fly ash as a low-cost adsorbent for various adsorption processes for adsorption of pollutants has been studied (Bello *et al.* 2011, 2013). Instead of using commercially activated carbon (CAC) or zeolite, a lot of researches have been conducted using fly ash for adsorption of different contaminants. However, adsorption performance and applicability of the ashes of fly ash strongly depends on fly ash origin and chemical treatment. Economic barriers have to be overcome in terms of high value and high volume utilization. It has been reported that the chemically modified coal fly ash showed larger specific surface area and higher pore volume with low energy consumption, especially when soaked in acid solution (Saha & Datta 2009; Adegoke & Bello 2015; Bello *et al.* 2015a, 2015b), thus making it a good candidate for different pollutants sequestration with an enhanced good adsorption capacity (Wang *et al.* 2005a, 2005b; Wang & Wu 2006).

However, despite positive uses of fly ash, the rate of production clearly far outweighs consumption (Figure 1). For the remaining material, disposal practices involve holding ponds, lagoons, landfills and slag heaps, all of which can be regarded as unsightly, environmentally undesirable and/or a non-productive use of land resources, as well as posing an on-going financial burden through their long-term maintenance. Furthermore, for those coal power plants located in urban areas, finding disposal sites is becoming increasingly more difficult. With competition for limited space and tightening of regulations on surface water and ground water discharge, any waste resulting from fly ash disposal sites must be well managed, so that local surface and ground water supplies are protected. This can cause significant economic burden to achieve the necessary water and land management. These factors have prompted researchers to look for alternative usages for fly ash other than the cement and construction industry thus finding the most suitable techniques for its valorization as adsorbent.

The importance of beneficiation in the utilization of fly ash for a particular application cannot be neglected (Figure 1(b)). Beneficiation techniques are used to influence the characteristic of fly ash in order to optimize its utilization, increase its value and minimize disposal cost. These techniques aid researchers in investigating the properties of fly ash and how it can be improved to produce a quality controlled fly ash product for removal of organic compounds (OCs) and also for other higher value applications in the polymer and ceramic industries (Bada & Vermaak 2008; Rajwar & Pandey 2014). The knowledge of fly ash mineralogy, the degree of the unburned carbon in fly ash and the quality needed in the market place are supreme in creating opportunities for research into the modification and exploitation of the unique chemistry of fly ash (Wang *et al.* 2004).Therefore, the study on the importance of beneficiation of fly ash had lead to comprehensive information regarding the feasibility of fly ash for adsorption process. It has been confirmed that the utilization of fly ash would solve both the disposal problem and served as a cheaper material for adsorption of water pollutants (Singh & Kolay

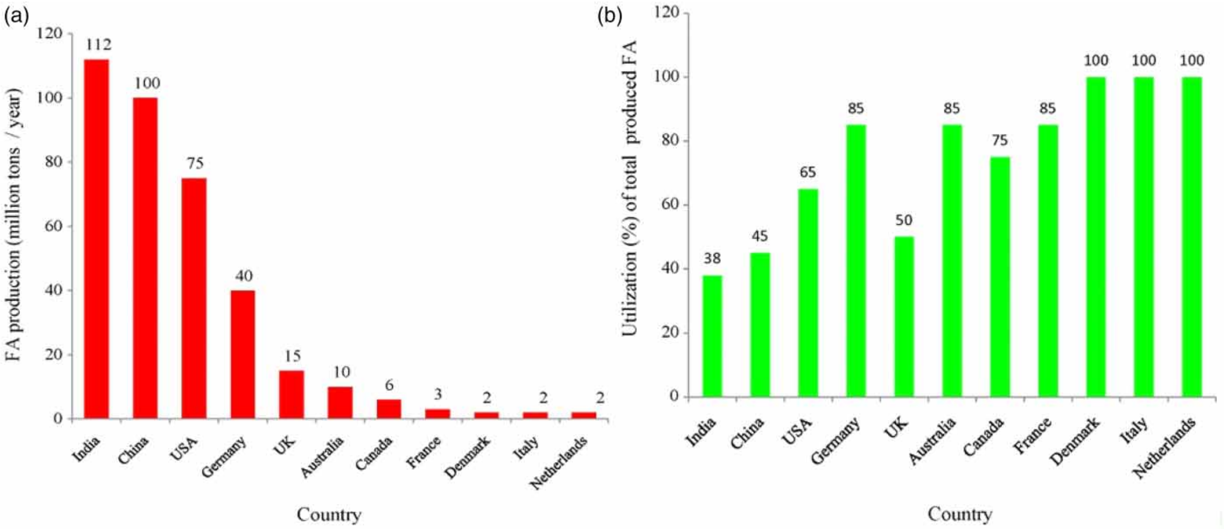

Figure 1 | (a) Fly ash production (million tonnes/year) in different countries (plots present data from the source: http://www.tifac.org.in) and (b) utilization (%) of total produced fly ash in different countries (plots present data from the source: http://www.tifac.org.in).

2002). Adsorption, which is a surface phenomenon that depends on the higher specific surface area, narrow particle size distribution and the porosity of adsorbent has been investigated (Kao *et al.* 2000).

Fly ash analysis and characterization

Physical and chemical analyses of the fly-ash have been reported (Rajwar & Pandey 2014). Figure 2 shows results of fly ash particle size distribution. The investigation reveals that most of the particles present in the fly ash are spherical in shape with a relatively smooth surface grain. It has been reported that the sub-angular and spherical particles with relatively smooth grains consisting of quartz, while clusters of iron (Fe-Oxide) particles formed due to partial decomposition of pyrite and with dark quartz inclusions. Similar results were obtained from the investigation conducted on Sasol ashes (Matjie *et al.* 2005).

Fly ash is characterized by quartz, mullite, subordinate hematite and magnetite, carbon, and a prevalent phase of amorphous aluminosilicate (Sokol *et al.* 2000; Hall & Livingston 2002; Mishra *et al.* 2003; Koukouzas *et al.* 2006). The abundance of amorphous aluminosilicate glass, which is the prevalent reactive phase, is what makes fly ash an important source material in zeolite synthesis. Fly ash cannot be properly used, both in cement manufacturing and in environmental application, without an in-depth knowledge of its mineralogical and chemical characteristics. So far, there have been lots of publications dealing with the morphological characterization of this material using scanning electron microscopy technique equipped with backscattered and secondary electron detectors and coupled with energy dispersive X-ray spectrometer (SEM-EDS) (Sokol *et al.* 2000; Kutchko & Kim 2006). The thermal analysis (TG/DTA) (Li *et al.* 1997) and the X-ray powder diffraction (XRD) (Ward & French 2006) have been carried out in order to gather the compositional information. The use of XRD and Fourier transform infra red spectroscopy (FTIR) (Vempati *et al.* 1994) in order to identify and quantify glassy materials contained in fly ashes was reported.

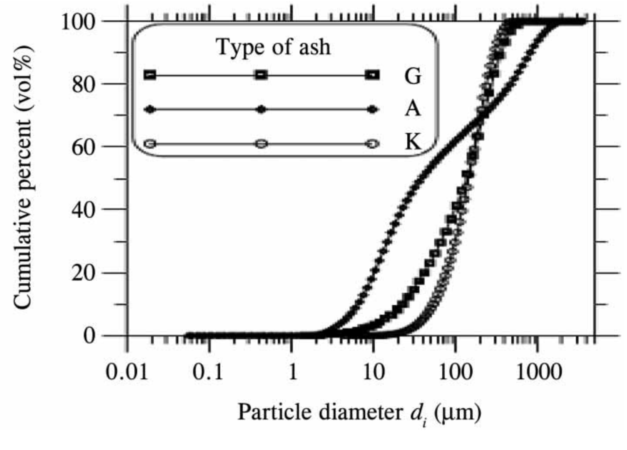

Figure 2 | Particle size distribution of tested fly ashes (Rajwar & Pandey 2014).

Fly ash application is also closely related to its chemical composition. In fact, a large amount of potentially hazardous leachable elements (Brindle & McCarthy 2006; Jegadeesan *et al.* 2008) restricts the application of this material. Recently, numerous scientists have gone extra miles in finding the alternative use to the characterized fly ash by converting this product (fly ash) to more eco-friendly material that can be use in environmental remediation (Kutchko & Kim 2006; Weng & Pan 2006; Saha & Datta 2009).

Leaching behaviour of fly ash in water system

Utilization of fly ash in water involves the potential leaching of some elements into water. This creates a problem of secondary environmental pollution. It was found that the surface layer of fly ash particles, probably microns in thickness, contain a significant amount of readily leachable material which is deposited during cooling after combustion. Therefore, the charge on the surface of fly ash particle and formation of the diffuse double layer plays a significant role in leaching. The elements present were divided into two groups on the basis of their concentration dependence on particle size. Results of the analysis by particle size indicates that the elements Mn, Ba, V, Co, Cr, Ni, Ln, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg and S are usually volatile to a significant extent in the combustion process. The volatility for these elements is inversely proportional to the particle size. Elements, such as Na, Mg, K, Mo, Ce, Rb, Cs and Nb appear to have a smaller fraction volatilized during coal combustion (Prasad *et al.* 1996). Here the volatility is directly proportional to particle size. The elements Si, As, Fe, Ca, Sr, La, Sm, Eu, Tb, Py, Yb, Y, Se, Zr, Ta, Na, Th, Ag and Zn are either not volatilized or may show minor trends which are related to the geochemistry of the mineral matter. The volatility of trace elements increased from a larger particle size to a smaller particle size which establishes an inverse relationship of volatility and particle size (Fisher *et al.* 1976).

Studies have revealed that only about 1–3% fly ash material is soluble in water with lignite fly ashes having a higher proportion of water soluble constituents (Keyser *et al.* 1978). The leaching of major elements from coal fly ash has been studied (Mattigod *et al.* 1990). Analysis of water extracts (Elseewi *et al.* 1980; Menon *et al.* 1980) showed that the principal cations in water extracts are calcium and sodium whereas anions are dominated by OH^-, CO_3 with aqueous extracts of the ash nearly saturated with $Ca(OH)_2$. The alkalinity and acidity controlled the extractability of elements like As, B, Be, Cd, Cr, Cu, F, Mo, Se, V and Zn. Aqueous extracts of an acidic fly ash contained concentrations of Cd, Co, Cu, Mn, Ni, Zn, As, B, Be, Cd, F, Mo, Se and V (Dressnen *et al.* 1976; Eisenberg *et al.* 1986). Leachate waters can have markedly different compositions, depending on the surface of fly ash, flue gas process conditions design of combustion systems and whether lime or lime stone injection processes were implemented for desulfurization. Total dissolved solid concentrations may vary from hundreds to tens of thousands of milligrams/liter. Even a small sample can show marked differences in leachate water chemistry, depending on reaction time and water/solid ratio in batch equilibrations or with column length and flow rate in a dynamic leaching test. The mineral and glass phases that constitute fly ash material are formed over a wide range of temperatures in the furnace environment. All these phases are unstable. They dissolve and then precipitate as stable and less soluble secondary phases. The primary phases even though highly soluble especially in water are dissolved very slowly as they are trapped in the glass and crystalline alumina silicates. Secondary hydrous aluminosilicate products are shown to be very insoluble (Hansen *et al.* 1984) and build up on rinds on the surfaces of primary phases. The dissolution of primary phases is slowed down as the mass transport of ions and water between phases becomes diffusion controlled.

However, a complex mixture of OCs is also associated with fly ash particles. The OCs identified in fly ash extracts include known mutagens and carcinogens. There are leaching procedures for the dissolution of the OCs of fly ash in 30–40% hydrogen peroxide, concentrated nitric acid under microwave conditions, or benzene. However, this chemical treatment also leaches components associated with both organic and inorganic compounds in fly ash. For example, some unstable minerals from the chloride, sulfate, sulfide, oxide, and carbonate classes may be leached, destroyed, or altered during this procedure. Formations of artificial minerals and phases such as oxyhydroxides, calcium oxalate, nitrates, and others are also possible. Hence, such minerals are not available or actual in the fly ash residue for any future mineralogical study. On the other hand, portions of organics may remain in the residue, because of the less soluble behaviour or when the solvent cannot contact with organics encapsulated in other inorganic matrixes (especially glass). There are traces of polycyclic aromatic hydrocarbons (PAHs) present in the coal fly ash, typically up to 25 mg/kg. Due to the low solubility, the leachate from coal fly ash contains very low concentrations of PAHs.

Many important aspects of the leaching behaviour of fly ash have been covered by a number of researchers (Pawar & Nimbalkar 2012). Therefore, it is suggested that the following measures should be taken before its use as adsorbent for water treatment:

(1) leaching behaviour test for the investigated water system;
(2) forced extraction of mobile substances from fly ash;
(3) immobilisation of mobile metals and other elements; and
(4) destruction of persistent organic pollutants.

To this end, concern about environmental protection has increased over the years from global point of view. In the past decades, the exponential population and social civilization growth changes in the productivity and consumption habits, increasingly affluent lifestyles, resource use, and continuing development of industrial technologies has been accompanied by the rapid generation of this industrial solid wastes, which create the most intransigent paradox around the world (Nagano *et al.* 2000; Benıtez & Lozano 2003; Renou *et al.* 2008; Montagnaro & Santoro 2009). To invalidate this critical trend, alleviation technologies such as conversion process and utilization have been reported during the last decades. Among the numerous processes, production of activated carbon from fly ash for adsorption of these pollutants is of great importance in pollution control and environmental conservation. There is a significant trend in recycling of waste materials and converting it to usable and valuable materials. One of these waste materials is coal fly ash. The disposal of the large amount of fly ash has become a serious environmental and economic problem (Li *et al.* 2006; Ahmaruzzaman 2010). One approach to deal with fly ash waste is to convert it to geopolymer, which is not only effective for pollutant removal, but also helps in solving the problem of ash accumulation as an industrial waste product.

Application and performance of fly ash based adsorbents for scavenging of organic contaminants

Removal of phenol and its derivatives

Phenolic pollution due to wide distribution and detection of phenol in the effluent of various industrial operations is a very important area of research, since phenolic wastewater is harmful for aquatic and human life. According to the standard set by United State Environmental Protection Agency (USEPA) surface water must contain less than 1 μg/L (Nor *et al.* 2010) phenol whereas effluents discharged in water bodies contain 3–10,000 mg/litre of phenol which is objectionable and toxic to animal and plant life (Srivastava *et al.* 2006).

Phenolic compounds had been reported to be removed very effectively using fly ash as adsorbent. Fly ash adsorbed 67, 20, and 22 mg/g for phenol, chlorophenol, and 2,4-dichlorophenol, respectively, for the highest water phase concentrations used (Ahmaruzzaman 2009). Various other works were also reported for the removal of phenol on fly ash and the effects of the most influential variables have been extensively treated and reviewed for ACs and low cost adsorbents by other researchers (Sarkar *et al.* 2003; AbdulLatif 2007; Pehlivan & Cetin 2008; Ahmaruzzaman & Gayatri 2010).

Removal of OCs

The presence of OCs are known as harmful pollutants because of their toxic, malodorous, mutagenic, and carcinogenic nature. These harmful products are produced or emitted from a variety of small and medium size industries in which adhesives, preservatives, paint, plastic, and solvent are manufactured and applied (Balathanigaimani *et al.* 2008). Among OCs, chlorinated volatile organic compounds (CVOCs) are common industrial solvents and by-products from the manufacture of chlorinated chemicals. These compounds are environmentally hazardous, often carcinogenic and mutagenic (Liu *et al.* 2010a, 2010b, 2010c), and some of them contribute to both ozone depletion and the greenhouse effect (Saral *et al.* 2009). In recent years, increasing environmental awareness has promoted stricter regulations of industrial actions. Therefore, the abatement of VOCs destruction is necessary, and the research on abatement of VOCs has drawn more and more attention. Several techniques have been developed for the abatement of VOCs, such as adsorption (Shim *et al.* 2006), condensation (Zhen *et al.* 2006), membrane separation (Wang *et al.* 2011), thermal or catalytic oxidation (Aranzabal *et al.* 2009), and biological treatments (Kocamemi & Cecen 2009), of which the adsorption technique is considered as a safe, economical, and efficient method, which can even remove trace amount of VOCs in atmosphere. In the adsorption technique, an adsorbent plays a key role in improving efficiency of VOCs abatement. Activated carbons and zeolites have been widely used to remove CVOCs. However, these traditional adsorption materials have some disadvantages in practice, such as low adsorption capacity, fire risk, and always suffering from the difficulty of desorption. Many authors have utilized fly ash to remove different organic acids (Albanis *et al.* 2000). More importantly, Bada & Vermaak 2008 reported the crack generated by the corrosion of the outer layer of the fly ash, thus leading to a chemical reaction that exposed the inner constituents of the fly ash thereby increasing the micro-pore volume.

Removal of dyes

Dyes are natural or synthetic OCs that have been used for colouring different types of materials for thousands of years. Synthetic dyes have been used extensively recently due to their low cost, bright colours, resistance to fading, and ease of use. This extensive use along with a high level of industrial production (e.g. textile, paper and pulp, dye and dye intermediates, pharmaceutical, tannery, and Kraft bleaching, etc.) has led to pollution of natural water resources and wastewater treatment systems (Bafana *et al.* 2011). One of the biggest sources of this type of pollution worldwide is wastewater from the textile industry. Release of the coloured waste into the environment is undesirable because it affects the esthetics, the water transparency, and the gas solubility of water bodies. Moreover, most of these dyes cause allergic reactions, dermatitis, skin irritation and also lead to mutations and cancer in humans (Adegoke & Bello 2015). Due to the worldwide concern about water pollution, global regulations have become more stringent (Adegoke & Bello 2015); as a result of this, effluents from dye manufacturing must be treated carefully before they are discharged. This has resulted in an increased demand for eco-friendly and economic technologies for removing dyes from aqueous effluent and various technologies have been developed for this purpose (Bello *et al.* 2013).

Numerous works have been published with the primary goal being the investigation of removal of different pollutants (either in gas or liquid medium) using adsorbent materials (Hessel *et al.* 2007; Kara *et al.* 2007; Sapkal *et al.* 2012; Kyzas *et al.* 2013; Bello *et al.* 2015a, 2015b). However, the structure and 'philosophy' of adsorbents used are not the same during the years. The first obvious change from past to present was the discovery of synthetic dyes. These dyes are cheaper to produce, brighter, more colour-fast, and easier to apply to fabrics. Scientists have formulated gorgeous new colours, and synthetic dyes have become obsolete for most applications. No doubt, this bright coloured material has changed the world; however, the chemicals used to produce dyes are often toxic, carcinogenic, or even explosive (Sharma *et al.* 2011; Adegoke & Bello 2015). Among the different pollutants of aquatic ecosystems, dyes are a major group of chemicals (Namasivayam & Kavitha 2002; Goyal *et al.* 2004; Attia *et al.* 2008). Since many industries with products such as textiles, leather, cosmetics, paper, printing, plastics, etc., use many synthetic dyes to colour their products. Thus, effluents from these industries contain various kinds of synthetic dyestuffs. For instance, dyes used in the textile industries are classified into three classes: (a) anionic (direct, acid, and reactive dyes); (b) cationic (all basic dyes); and (c) non-ionic (dispersed dyes). Basic and reactive dyes are extensively used in the textile industry because of their favourable characteristics of bright colour, being easily water soluble, cheaper to produce, and easier to apply to fabric (Karcher *et al.* 2002; Karadag *et al.* 2007; Purkait *et al.* 2007). The feasibility of using fly ash as an alternative to activated carbon was re-examined recently for colour removal from synthetic dye solutions (Chatterjee *et al.* 2010; Bello *et al.* 2011; Sahoo *et al.* 2013). Table 1 presents a brief comparison of previous studies on dye adsorption onto fly ash.

Removal of pesticides

Generally, pesticide is featured by its unique chemical structures developed to mimic and substitute for specific molecules to the targeted pests (Gavrilescu 2005). Since pesticide is commonly used in agriculture sector to control wide range of broad leaf weeds and grasses in plantation crops, such as sugar cane, oil palm, cocoa and rubber. The toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating our environment (Hameed *et al.* 2009). Therefore, the removal of pesticides from water is one of the major environmental concerns these days. Leaching of chemical fertilizers and pesticides, applied to agricultural and forest land, is one of the main reasons for organic pollution in several water streams. The removal of the pesticides by conventional biological treatments has proven to be ineffective, while activated carbons was more effective. Thus, activated carbons are applicable to a wide range of processes for the removal of OCs in water (Li *et al.* 2002; Moreno-Castilla 2004).

Factors affecting fly ash adsorption performance

Paramount factors affecting adsorption performance is the effect of contact time and initial concentration of pollutants. The initial concentrations of pollutants have a strong effect on the adsorption capacity of various industrial waste materials. Generally, adsorption capacity increased with increased initial concentration of pollutants. The initial concentration provides an important driving force to overcome all mass transfer resistance of pollutants between the aqueous and solid phases. The removal of pollutants to reach/attain the equilibrium also varied with contact time. Another crucial factor is the effect of pH. Here, the solution pH has a pronounced influence on the adsorption of pollutant charges. In a certain pH range, most pollutant adsorption increases with increasing pH up to a certain value and then decreases with further increase in pH. This is readily explained by the adsorption mechanism. Therefore, there is a favorable pH range for the adsorption of every pollutant on a certain industrial waste material. The effect of pH may also be accounted in terms of pH_{zpc} of the adsorbent, at which the adsorbent is neutral. The surface charge of the adsorbent is positive when the media pH is below the pH_{zpc} value, while it is negative at a pH over the pH_{zpc}.

In addition, effect of particle size also plays an important role in adsorption technology. Intra-particle diffusion study shows that particle size of the waste materials used greatly influences the adsorption rate. Decrease in particle size would lead to increase in surface area and then increase in the adsorption capacity at the outer surface of the waste materials. Besides adsorption at the outer surface of the waste material, there is also a possibility of intra-particle diffusion from the outer surface into the pores of the material. The diffusional resistance to mass transfer is higher for large particles. Due to various factors, such as diffusional path length or mass transfer resistance, contact time, and blockage of some diffusional path, most of the internal surface of the particle may not be utilized for adsorption; consequently, the adsorption efficiency may become low.

The adsorption capacity of waste materials depends largely on the surface activities – in other words, specific surface area available for solute surface interaction, which is accessible to the solute. It is expected that adsorption capacity will be increased with a larger surface area. In other words, smaller particle size increases the adsorption capacity.

Lastly, the effect of ionic strength cannot be overemphasized since ionic strength of the pollutant is a general property of the solution affecting the affinity between the solute and the aqueous phase. This is one of the important factors which influence the aqueous phase equilibrium. Generally, adsorption decreases with increasing ionic

Table 1 | Comparison of dye adsorption on fly ash

Dye	Fly ash type	Adsorption capacity (mol/g)	Temperature (∘C)	Adsorption isotherm	Kinetic model	References
Methylene blue	Coal FA	14.4×10^{-5}	25	Langmuir		Viraraghavan & Ramakrishna (1999)
Crystal violet	Coal FA	9.76×10^{-5}	25	Freundlich	Lagergren first-order	Mohan *et al.* (2002)
Rosaniline hydrochloride	Coal FA	1.35×10^{-5}	25	Freundlich	Lagergren first-order	Mohan *et al.* (2002)
Methylene blue	FA-F	1.89×10^{-5}	22	Langmuir		Janos *et al.* (2003)
Rhodamine B	FA-F	1.15×10^{-5}	22	Langmuir		Janos *et al.* (2003)
Egacid orange II	FA-F	2.364×10^{-4}	22	Langmuir		Janos *et al.* (2003)
Egacid Red G	FA-F	1.405×10^{-4}	22	Langmuir		Janos *et al.* (2003)
Egacid yellow G	FA-F	5.2×10^{-5}	22	Langmuir		Janos *et al.* (2003)
Midlon Black VL	FA-F	3.3×10^{-5}	22	Langmuir		Janos *et al.* (2003)
Acid Blue 29	FA	3.25×10^{-6}	–	Freundlich		Ramakrishna & Viraraghavan (1997)
Acid Blue 9	FA	5.43×10^{-6}	–	Freundlich		Ramakrishna & Viraraghavan (1997)
Acid Red 91	FA	2.34×10^{-6}	–	Freundlich		Ramakrishna & Viraraghavan (1997)
Acid Red 1	FA	7.26×10^{-6}	–	Freundlich		Ramakrishna & Viraraghavan (1997)
Congo red	FA-C	4.47×10^{-5}	20	Freundlich	Pseudo-second-order	Acemioğlu (2004)
Methylene blue	FA-F	3.47×10^{-6}	–	Langmuir		Woolard *et al.* (2002)
Methylene blue	FA-F	1.4×10^{-5}	30	Redlich-Peterson		Wang *et al.* (2005a, 2005b)
Methylene blue	FA-HNO_3	2.2×10^{-5}	30	Redlich-Peterson		Wang *et al.* (2005a, 2005b)

strength of the aqueous solution. This effect may be ascribed to changes in the pollutant activity, or in the properties of the electrical double layer. According to surface chemistry theory, when two phases, e.g. waste particles and contaminants species in aqueous solution, are in contact, they are bound to be surrounded by an electrical double layer owing to electrostatic interaction. Thus, if the increase in adsorption is significantly a function of electrostatic attraction, adsorption decreases with increase in ionic strength.

Problems associated with using fly ash as adsorbents and its current challenges

Fly ash, the byproduct of thermal power plant is gaining attention as it is generated in large quantities as waste material during combustion process globally. It is estimated that 500 Mt of fly ash is produced worldwide annually (Ahmaruzzaman 2010). In India, generation of fly ash from coal based thermal power plants is 131 Mt/year and it is expected to increase to 300–400 Mt/year by 2016–2017 (Haque 2013). The main problem with the fly ash is its generation in huge quantity (Figure 1(a)). As per the estimates proposed, its generation is expected to increase to about 1000 million tonnes by 2032 (Annual Report 2012–2013). Numbers of utilization techniques are available for usability of fly ash but effectiveness of such use is property dependent. The ultimate fate of fly ash is majorly associated with its disposal as landfill but this provokes environmental as well as economical concerns. Hence, it becomes necessary to search for an effective method which answers to these concerns. Application of fly ash in different industrial sectors increases markedly, but still the generation of fly ash is far greater than its utilization (Figure 1(a) and 1(b)). Therefore, efforts are being directed towards innovative, environmentally friendly applications which make best possible use of this abundantly available material. However, probable environmental impacts related to fly ash utilization have been extensively explored and are well understood.

Vulnerability of heavy metals leaching from the ashes is relatively low and therefore the risks associated with the release of these metals into the environment do not exceed beyond permissible level (Maurya *et al.* 2008).

Coal-based thermal power plant in the world is facing serious problems of handling and disposal of fly ash (Pandian 2004). The bulk of fly ash is stockpiled in slurries as ash dam (Mattigod *et al.* 1990; Abbott *et al.* 2001). Thus, massive quantity of fly ash is dumped in ash pond leading to grave environmental degradation because of leaching of toxic elements to the surrounding water bodies. During the dry season, it is carried by air current from the ash pond causing severe respiratory diseases in the surrounding population. At present, bulk utilization of unused ash is a serious issue for power plant authorities due to the requirement of large land area for the disposal of fly ash (Das *et al.* 2012) and it continues to contribute to various environmental, economic and social problems (Bhattacharjee & Kandpal 2002; Basu *et al.* 2009). The amount of unburned carbon, mineralogy and the quality of fly ash needed in the market are supreme in creating opportunities for new research into the modification and exploitation of the unique chemistry of fly ash (Mane *et al.* 2007).

Overcoming barriers of fly ash utilization

There are a number of technical, economic, institutional, and legal barriers to the use of large quantities of fly ash. Technical and economic barriers are not mutually exclusive in that technological advancements usually result in economic feasibility. Principal technical barriers include issues related to fly ash production, specifications and standards, material characterization, product demonstration and commercialization, and other user related factors. An economic barrier to increase the use of fly ash is a key among all factors affecting by-product use. With proper economic incentives, other barriers to increased use of fly ash can be overcome (Ugurlu *et al.* 2005). For coal-burning electric utilities, the revenues from the sale of fly ash are often insignificant. The high cost of transportation of low unit-value fly ash and competition from locally available natural materials are the most important economic barriers.

Among institutional and legal barriers are the lack of knowledge of potential ash uses, sporadic data on environmental and health effects, compositional inconsistencies in the products, belief that other raw materials are readily available, lack of State guidelines and viewpoint of the industry and Environmental Protection Agency (EPA) regulations and procurement guidelines are too complicated and rigid rather than being general guidelines for use (Pawar & Nimbalkar 2012).

An American Society for Testing and Materials (ASTM) subcommittee under the Committee E-50 on Environmental Assessment, on which the US Geological Survey (USGS) is represented, was recently formed to address the question of standards and definitions of coal and coal combustion products (CCPs)-related terms. Subcommittee members evaluated the latest draft of the definition document. Recommendations were submitted to the committee for action in 2001. This draft calls for the change of CCPs to coal combustion by-products to iterate the ideal definition of a product, which is the principal reason for a process. It is argued that coal is burned to produce energy, not ash (Wang & Wu 2006). Therefore, energy is the product of coal-burning processes; anything else is a by-product. Concerned industry and government representatives, scientists, and engineers have formed a number of national and international organizations to address the removal of barriers to the use of fly ash.

Fly ash transportation cost for reclamation of abundant mine and road construction is a major constraint. Restriction of excavation of earth for filling low-lying areas and construction of embankment within 200 km radius of a thermal power plant is essential. Furthermore, there should be a mandatory condition in the policy legislation to use fly ash in place of soil for such applications. Lack of awareness on the advantages of fly ash based products among end-users is limiting new initiatives and market potential. There should be an integrated approach by the coordination of technologists, architects and manufacturers for the production of superior quality fly ash based products to meet consumer acceptability and increased marketability. In addition, in association with scientists, policy makers and fly ash generators, awareness of the quality parameters and beneficial effects of fly ash based building materials and its utility should be made clear to the general public for mass consumption and effective utilization of fly ash. There is a production of huge quantity of fly ash followed by emission of green house gases, thereby significantly curbing global warming (Wang & Wu 2006). Also, similar situations exist in several developed and developing countries. Hence, to comply with environmental requirements, serious efforts are to be made to tackle this alarming situation of fly ash management to reduce the adverse effect on environment, ecology and other future hypothesis by finding remedial measures for social development. Cost benefit analysis of fly ash versus conventional building materials are needed to be thoroughly evaluated for the concrete recommendation for maximizing the use of fly ash. Barriers to utilization of fly ash on land occur in marketing, transport and through its potential as leachates containing trace elements. These are overcome by various means in the utilization sectors. It is essential to follow best engineering practices to ensure that there are no environmental risks.

Regeneration/recovery studies of fly ash

Regeneration is a very important aspect of the adsorption from economic and environmental point of view. It actually answers various questions and anxieties as to what would happens to the adsorbent after adsorption in order not to render the whole findings useless since such adsorbent may contain toxic adsorbates. The disposal of adsorbent is one of the problems associated with the adsorption processes. Regeneration can reduce the need for new adsorbent and also reduce the problem of disposal of used adsorbent. For instance, approximately 500 million tons of fly ash is discharged per year throughout the world. Since fly ash has a pozzolanic property after reaction with lime (Inada *et al.* 2005), about 20% of fly ash is used as building materials. Fly ash is used as a supplementary cementitious material (SCM) in the production of Portland cement concrete. A SCM, when used in conjunction with Portland cement, contributes to the properties of the hardened concrete through hydraulic or pozzolanic activity, or both. However, the remaining fly ash disposed in landfill cause threats to the environment due to its fine structure and toxic elements. Disposal of fly ash is a universal problem and has become a key concern globally. Fly ash obtained after it had been used in effluent treatment plant for removal of organic matter is obviously rich in organic content. Currently, fly ash is disposed in the form of slurry in fly ash ponds. The major environmental challenge from fly ash dumping, discharge and disposal is organic pollution of surface and ground water. Fly ashes precipitated from air by rain thereby find their way into the surface water unless fly ash ponds are properly sealed.

There are several well-established methods for the regeneration of spent CAC of which fly ash is considered as one of them. Despite a notable success of these techniques applied to a number of adsorbates, yet, regeneration efficiency depends on the solubility of the adsorbed substances and the effect of pressure on the chemical structure of carbon. Also, such a large investment in high-pressure equipment makes the method rather expensive. As a result of these major drawbacks, a number of other alternative regeneration methods are hot topics of investigation. Some of these methods can be operated *in situ* and has offered not only the advantage of oxidizing organic contaminants in the anode, but it also allows recovering active adsorbing site of exhausted AC. Several authors have reached a consensus that increasing the period of regeneration and the current used usually resulted in an increase of regeneration efficiency (Snyder & Leesch 2001; Zhang *et al.* 2002; Brown *et al.* 2004a, 2004b; Garcia-Oton *et al.* 2005; Zhou & Lei 2006; Purkait *et al.* 2007; Han *et al.* 2008; Weng & Hsu 2008).

CONCLUDING REMARKS

Currently, researches are now focused on how to improve the ability of fly ash through proper modification and regeneration techniques in order to increase its adsorption rate. The use of commercially available activated carbon for the removal of the pollutants can be replaced by the utilization of inexpensive, effective, and readily available fly ash as adsorbents. More studies should be carried out to better understand both the process and mechanisms of using low-cost adsorbent materials to demonstrate the technology effectively. Disposal of the pollutant-laden industrial waste is again a big problem. If this is left undone, a serious question such as what happens to the ash after adsorption would arise, thus rendering the whole findings useless since such ash contains toxic adsorbates, then it may present a worse problem than the ash on its own, thus leaving a serious concern. The ash with pollutants can still be used in cement or concrete, brick production and as a filling in road works or for another purposes, it is a valorization that is worthwhile. Therefore, more tangible research should be conducted on the various methods to ensure environmental friendly, safe disposal and optimization of spent adsorbent of pollutant laden adsorbents.

Literature studies reviewed above illustrates that adsorption process can be considered an efficient treatment for the removal of emerging contaminants from water. It facilitates higher percentage removal; also, being a physical process, it does not generate by-products formation, which could be more toxic than parent compounds. It is obvious that adsorption process is encompassed in an integrated treatment system which involves many factors, such as available space for the construction of treatment facilities, waste disposal constraints, desired finished water quality, and capital and operating costs. All these factors led to the achievement of the optimal operating conditions that promote high efficiencies. This is a renewable approach since fly ash activated carbons are derived from industrial solid wastes: its use for adsorption of these pollutants is of great importance in pollution control and environmental conservation.

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