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Recent trends in the use of fly ash for the adsorption of pollutants in contaminated wastewater and soils: Effects on soil quality and plant growth

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Abstract

Fly ash is one of the largest types of industrial wastes produced during the combustion of coal for energy generation. Finding efficient and sustainable solutions for its reuse has been the subject of substantial research worldwide. Here, we review the recent research data related to (i) the use of fly ash as a low-cost adsorbent for pollutants in wastewater and soils and (ii) its implications in soil–plant system. Fly ash showed prominent adsorption capacity for pollutants in water especially when it was activated or applied in composites. In addition to direct pollutant binding in soils, fly ash can enhance the soil pH indirectly increasing metals' immobilization reducing their plant uptake. Its non-selective adsorptive nature may lead to the co-adsorption of nutrients with pollutants which merits to be considered. Owing to its considerable nutrient contents, fly ash can also improve soil fertility and plant growth. The effects of fly ash on soil physico-chemical properties, microbial population and plant growth are critically evaluated. Fly ash can also contain potentially toxic contaminants (toxic metals, hydrocarbons, etc.) which could have harmful impacts on soil health and plant growth. Identifying the levels of inherent pollutants in fly ash is crucial to evaluate its suitability as a soil amendment. Negative effects of fly ash can also be addressed by using co-amendments, biological agents, and most importantly by an adequate calibration (dose and type) of fly ash based on site-specific conditions. Research directions are identified to promote the research regarding its use in wastewater treatment and agriculture.

Keywords Coal fly ash · Adsorption · Wastewater treatment · Environmental pollution · Soil remediation · Crop production

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Introduction

Coal is among the major sources of energy worldwide that covers over one third of electricity generation. According to the latest Key World Energy Statistics by International Energy Agency (IEA 2021), the share of coal in world electricity generation was 36.7% in 2019. Worldwide use of coal has been estimated to be about 7,700 million tonnes producing about 11 million tonnes of coal ash (Harris et al. 2020). The utilization rate of coal ash is, however, about 63% and the remaining amount is the waste being dumped in the environment (Harris et al. 2020). Coal fly ash is a powdered by-product of coal combustion which constitutes about 65–95% of the total generated ash making it one of the largest types of industrial waste (Jayaranjan et al. 2014). Due to its widespread abundance and varying composition, coal fly ash has been recognized among the most abundant and complex anthropogenic materials (Yao et al. 2015). Therefore, finding sustainable solutions for its disposal and reuse has received significant attention among

the scientific community and environmental agencies. Coal fly ash has demonstrated its potential as a valuable, high-volume input to manufacture building and construction materials. For example, concrete production recycles about 20% of the generated fly ash (Yao et al. 2015). Similarly, fly ash may also be applied for road base construction, synthesis of environmental materials like zeolite, soil amendment, etc. (Ahmaruzzaman 2010). However, these uses are insufficient for the complete utilization of fly ash. Its improper disposal causes soil and water contamination posing serious threats to the environment and ecological cycles. In the future, rigorous restrictions for disposal sites, strict environmental regulations, decreasing availability of landfill areas, and growing costs of disposal are expected. Therefore, it is crucial to establish efficient and cost-effective strategies to utilize fly ash in an environment-friendly way.

In recent years, research concerning the environmental applications of fly ash has been the subject of numerous publications (Yao et al. 2015). Though a great amount of research data is available in this field (Gadore and Ahmaruzzaman 2021; Shaheen et al. 2014), a comprehensive review is still needed to explain the role of fly ash to adsorb contaminants in wastewater and soils along with a critical description of its implications in the soil–plant system. In addition to exploring the remediation potential of an amendment, it is also highly demanding to evaluate its impacts on soil's physicochemical properties, microbial activity, soil fertility, crop productivity, and plant growth. To cover this theme, this review is intended to compile the recent literature (mainly onward from 2015) regarding the applications of fly ash to decontaminate wastewater and soil via adsorption, and its implications in the soil–plant system. The massive production, lower cost, and high surface area of fly ash make it an attractive adsorbent material. In the first part of this review, we compile the research data related to its use for the remediation of contaminated water and soils. In addition to its decontamination capacity, fly ash also contributes in improving the soil health and quality owing to its structural constituents (nutrients, high lime content, etc.). This improvement has been evaluated in terms of soil's physicochemical properties, fertility, microbial community, plant growth and biofortification potential in the second part of this review. Besides the useful elements, fly ash may also contain significant amounts of potentially toxic elements and/or organic pollutants which could limit its application. A critical evaluation of the potential threats of fly ash to the soil system is also provided.

Characteristics of fly ash

The characteristics of fly ash dictate its subsequent use, efficiency, and disposal. It becomes, therefore, highly important to understand its physical, chemical, and mineralogical

characteristics before its application. Coal fly ash contains very fine particles (< 10 μm of average diameter) aggregated into cenospheres (hollow particles) of about 0.01–100 μm which become easily airborne (Shaheen et al. 2014). The majority of the coal fly ash has a specific gravity between 2.1 and 3.0. However, owing to the small size of its particles, fly ash exhibits a high surface area ranging from 170 to 1000 m^2 g^{-1} (Gadore and Ahmaruzzaman 2021). The blackish color of coal fly ash is produced by its carbon contents. The SEM/EDX characterization by Nath et al. (2016) showed that raw fly ash mainly contains alumino-silicate spherical grains varying in size between 1 and 15 μm (Fig. 1).

Regarding the chemical composition of fly ash, alumina, calcium, silica, and iron oxide (hematite, magnetite, and maghemite) are the major ingredients which are present in varying amounts (Fig. 1). The contents of iron oxides in fly ash can vary from 2 to 20% depending upon the type of the coal source (Jiao et al. 2021). Among these iron oxides, magnetite and maghemite are ferromagnetic in nature (Usman et al. 2018a), and, therefore, fly ash particles are highly magnetic in the presence of these iron oxides (Jiao et al. 2021). It is worth mentioning that the use of magnetic adsorbents can be advantageous as they can be quickly separated from the reaction medium by applying a magnetic field (Ajmal et al. 2020). Depending upon the mineral composition, coal fly ash is broadly categorized in following two groups:

o ***Class F fly ash***: When the total contents of silica, alumina, and iron oxide are higher than 70 wt.% of the raw fly ash, it is termed as class F fly ash. This is produced
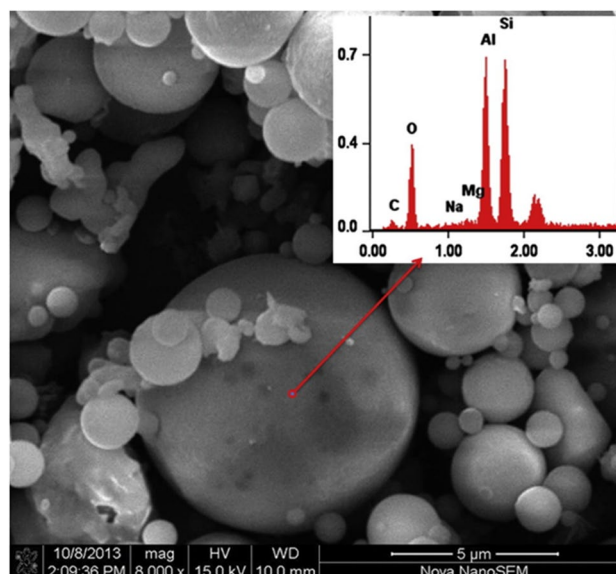

Fig. 1 Morphology of the fly ash characterized by SEM/EDX. This image is reproduced with permission from Ref. (Nath et al. 2016)

by burning anthracite and bituminous coal having < 10% of lime (Gadore and Ahmaruzzaman 2021).

p **Class C fly ash**: This is the type of fly ash that contains total contents of silica, alumina, and iron oxide in the range of 50–70 wt.%. This is formed by the combustion of low-quality coal like lignite and sub-bituminous having > 20% of lime (Gadore and Ahmaruzzaman 2021). Class C fly ash usually contains a higher quantity of alkalis and sulphates as compared to the Class F fly ash which is another difference between both classes (Ahmaruzzaman 2010). All these properties dictate the efficiency and role of fly ash for its subsequent use as elaborated in the next sections. The chemical composition of fly ash also affects its pH which varies significantly. For example, Riehl et al. (2010) reported that the pH of coal fly ash varies between 4.5 and 13.25, depending mainly on the contents of CaO and sulphur in the parent coal.

Regarding its nutrient contents, fly ash is a rich source of micro and macronutrients. It generally contains substantial amounts of silicon (Si), aluminum (Al), and iron (Fe) with a relatively high proportion of calcium (Ca), phosphorous (P), potassium (K), and sodium (Na) (Gadore and Ahmaruzzaman 2021; Shaheen et al. 2014). Fly ash usually contains negligible amounts of nitrogen due to its oxidation during the combustion process (Shaheen et al. 2014). Besides the elements that are necessary for plant growth, fly ash may also contain significant amounts of potentially toxic elements and/or organics which could limit its application (Cruz et al. 2017). However, compared to coal fly ash, toxic elements are not usually present in biomass ash (Gadore and Ahmaruzzaman 2021). Moreover, soil's enrichment with toxic elements can be negligible as coal fly ash is usually added in small amounts (Shaheen et al. 2014). The use of fly ash for several years in agricultural fields revealed that there is no harm of long-term application of fly ash to the soil, nevertheless, continuous monitoring should be sought (Hadas et al. 2021). Potential benefits and risks associated with the use of fly ash are described in the following sections.

Applications of fly ash for pollutant adsorption in water

It is highly demanding to decontaminate the polluted wastewater for its safe disposal in water bodies or agricultural fields (Anastopoulos and Kyzas 2014). There exist many technologies for wastewater treatment such as chemical precipitation, solvent extraction, membrane filtration, ion exchange, electrochemical removal, coagulation, etc. (Burakov et al. 2018). Most of these techniques are limited by high operational and maintenance costs, generation of toxic sludge, and complicated procedures involved in the treatment (De Gisi et al. 2016). Adsorption has been proven to be a viable technique to remove various pollutants from waste(water) owing to its low-cost, ease of operation, and high efficiency (Uddin 2017). Based on the concept of the circular economy, fly ash in raw or modified forms, may be used as efficient and low-cost adsorbents for the removal of various pollutants from aqueous solutions (Ahmaruzzaman 2010). This section describes the applications of fly ash-based materials (mainly onward from 2015) for the adsorption of toxic elements, dyes, and other miscellaneous pollutants.

It should be noted that accurate modeling of pollutants' removal from aqueous media relies on the adsorption isotherm, kinetics modeling, and thermodynamic evaluations (Anastopoulos and Kyzas 2014). The adsorption isotherms models provide information about the maximum adsorption capacity and may also contribute to identifying the interactions between adsorbent and adsorbate to some extent (Foo and Hameed 2010; Mahdieh et al. 2021). Kinetic studies facilitate in estimating the equilibrium time of the adsorption and kinetic modeling is used to calculate the adsorption rate, which is particularly important for potential upscaling of the treatments (Hubbe et al. 2019; Lima et al. 2021). Table 1 presents the most-common isotherm and kinetic models. Adsorption thermodynamics (the associated parameters (Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) Table 1)) is an integral component in the study of adsorption and plays a vital role in estimating adsorption mechanism (i.e., physisorption and chemisorption) (Tran et al. 2021).

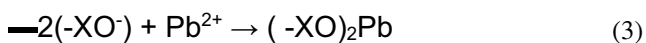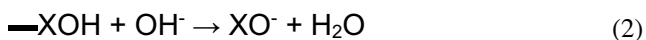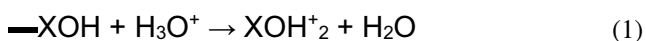## Fly ash-based adsorbents for the removal of toxic metals

The use of fly ash-based adsorbents has shown good potential to remove various potentially toxic elements. The best isotherm, kinetic model together with the maximum (in most cases) adsorption capacities are summarized in Table 2. For example, Tomasz et al. (2019) used fly ash to remove Pb(II) from aqueous media. Maximum adsorption efficiency of 97.4% was obtained using an initial Pb(II) concentration of 102 mg L^{-1}, adsorbent dosage of 5 g L^{-1}, and at pH of 4.4. Kinetic studies revealed that the removal was fast in the first 10 min of reaction and the equilibrium was reached at 15 min. Regarding the effect of pH, low adsorption was recorded at an initial pH of 2 that can be ascribed to the competition between hydrogen ions and Pb(II) for the same active sites in fly ash. With an increase in pH, the concentration of hydrogen ions was rapidly decreased that increased the amount of sorbed Pb(II). The pH of the solution affects the charge of oxides SiO_2, Al_2O_3 and others

Table 1 Isotherm, kinetic and thermodynamic equations (reproduced with permission from Ref. (Philippou et al. 2021))

Expression	Equation form	Parameters
Non-linear Langmuir (Langmuir 1918)	$q_e = q_m \frac{b_L C_e}{1 + b_L C_e}$	q_m(mg g^{-1}): saturated monolayer adsorption capacity b_L(L mg^{-1}): constant related to the energy of sorption and equilibrium constant
Non-linear Freundlich (Freundlich 1906)	$q_e = K_F C_e^{1/n}$	K_F: (mg g^{-1})(L mg^{-1})$^{1/n}$: Freundlich constant n:Freundlich constant
Non-Linear pseudo-first-order kinetic (Lagergren 1898)	$q_t = q_e(1 - e^{-k_1 t})$	q_t (mg g^{-1}): is the amount adsorbed at time t (min) k_1 (min^{-1}): is pseudo-first-order rate constant
Non-linear pseudo-second-order kinetic (Blanchard et al. 1984; Ho & McKay 1999)	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	q_t (mg g^{-1}): is the amount adsorbed at time t (min) k_2 (g mg^{-1} min^{-1}): is pseudo-second-order rate constant
Gibbs free energy	$\Delta G^0 = -RT \ln K$	Free energy change
Van't Hoff[*] (Lima et al. 2019b)	$\ln(K) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	Enthalpy change ($\Delta H°$) Entropy change ($\Delta S°$)

[*]It should be noted that the K equilibrium constant must be unitless (2019a, Lima et al. 2019b). C_e is the equilibrium concentration of the adsorbate (mg L^{-1}) in solution.

that are presented in fly ash. The ion exchange mechanism between hydrogen and Pb(II) ions can be explained by the Eqs. (1–3) presented below (Tomasz et al. 2019):

$$\text{—XOH} + H_3O^+ \rightarrow XOH_2^+ + H_2O \tag{1}$$

$$\text{—XOH} + OH^- \rightarrow XO^- + H_2O \tag{2}$$

$$\text{—2(-XO}^-) + Pb^{2+} \rightarrow (\text{-XO})_2Pb \tag{3}$$

where: X can be Si, Al or Fe.

In another study, coal fly ash was examined to remove Fe(II) (Orakwue et al. 2016). Adsorption equilibrium was achieved in 30 min and the mean free energy obtained from Dubinin–Radushkevich (D-R) isotherm model was estimated to be 0.0122 kJ mol^{-1}, indicating the adsorption as a physisorption process. It has been proposed that in addition to adsorption, iron hydroxide precipitation (Usman et al. 2012) can also be another mechanism behind Fe(II) removal (Orakwue et al. 2016). In another study, the removal of Cd(II) was examined using palm oil boiler mill fly ash as an adsorbent (Aziz et al. 2015). Kinetic studies revealed that 210 min were sufficient to reach the equilibrium while the optimum pH value for Cd(II) adsorption was 7. At pH ≤ 5, an electrostatic repulsion was reported between the positively charged surface of adsorbent and the cationic Cd(II), thus lowering the adsorption. In the pH range of 5–7, the electrostatic repulsive interactions became weaker and the availability of H$_3$O$^+$ reduces. Thus, adsorption is increased as a result of an electrostatic attraction between the positively charged metal ion and the partially negatively charged adsorbent surface. At a higher pH value (> 7), the adsorption capacity became constant, and the Cd(II) starts to precipitate as Cd(OH)$_2$. The EDX analyses before and after Cd

adsorption indicated the disappearance of some metal cations such as K$^+$ and Fe(II), suggesting the significant role of the ion-exchange mechanism in Cd(II) adsorption. Qiu et al. (2018) used hydrothermally modified circulating fluidized bed fly ash for Cd(II) adsorption. Optimum adsorption appeared at an initial pH of 6.2 and the equilibrium was achieved in 120 min. The rise of temperature from 298 to 318 K had a positive effect on the adsorption capacity which increased from 130.2 mg g^{-1} to 208.7 mg g^{-1}, respectively. Kinetic data showed that intra-particle diffusion was not the only adsorption rate-controlling step during the uptake of Cd(II). The authors concluded that the removal of Cd(II) at pH of 6.2 (the final pH was < 7.2) occurred predominately via adsorption. However, at an initial pH > 6.2 (the final pH was 8.5–8.9), both adsorption and precipitation processes took place simultaneously (Fig. 2).

Coal fly ashes from different thermal power plants were also examined for the adsorption of Cr(VI) (Naiya & Das 2016). For all fly ashes, the highest adsorption was achieved at pH = 2 and 4 h were sufficient to attain the equilibrium. The mean free energy obtained from Dubinin–Radushkevich (D-R) isotherm model was estimated to be 12.845–15.394 kJ mol^{-1}, indicating the chemical nature of the adsorption process. The thermodynamic study indicated that this process was spontaneous and endothermic. Microwave-assisted alkali modified fly ash was used for Cr(VI) removal in another study (Deng et al. 2018). The highest removal was recorded at acidic conditions (pH = 1) with equilibrium reaching in 1 h. The rise of temperature from 293 to 333 K negatively affected the adsorption capacity. In another interesting work, raw and mechanically activated fly ash were examined to adsorb Cu(II), Mn(II), Ni(II), Pb(II), and Zn(II) (Xiyili et al. 2017). The mechanical activation in the planetary ball mill led to a higher adsorption capacity by increasing the

Table 2 The maximum monolayer adsorption capacity and the best isotherm and kinetic models for the adsorption of various pollutants onto fly ash-based adsorbents

Adsorbent	Pollutant	Maximum removal capacity	Dominant isotherm / kinetic model	Ref
Metals				
Fly ash	Pb(II)	51.98 mg g^{-1} at 296 K (From Langmuir isotherm $R^2 = 0.971$)	Freundlich / pseudo-second order	(Tomasz et al. 2019)
Raw and mechanically activated fly ash	Pb(II)	Raw:108.9 mg g^{-1}, Mechanically activated: 110.3 mg g^{-1}, at room temperature (obtained from kinetic studies)	Langmuir / pseudo-second order	(Xiyili et al. 2017)
Coal fly ash	Fe(II)	56.63 mg g^{-1} at 303 K (obtained from the effect of initial concentration study: initial concentration 3194 mg L^{-1}, v = 100 mL, adsorbent dose = 4 g)	Temkin / pseudo-second order	(Orakwue et al. 2016)
Palm oil boiler mill fly ash	Cd(II)	15.82 mg g^{-1} at 303 K (From Langmuir isotherm $R^2 = 1.0000$)	Langmuir / pseudo-second order	(Aziz et al. 2015)
Hydrothermally modified circulating fluidized bed fly ash	Cd(II)	134.9 mg g^{-1} at 298 K (From Langmuir isotherm $R^2 = 0.9965$)	Langmuir / pseudo-second order, Boyd	(Qiu et al. 2018)
Thiol Functionalized Coal Fly Ash	Cd(II)	92.59 mg g^{-1} at 298 K (From Langmuir isotherm $R^2 = 0.9904$)	Langmuir / pseudo-second order	(Dash et al. 2017)
Coal fly ashes from different thermal power plants	Cr(VI)	21.67 to 28.70 mg g^{-1} at 303 K (From Langmuir isotherm $R^2 = 0.9530$–0.9790)	Freundlich / pseudo-second order	(Naiya & Das 2016)
Microwave-assisted alkali modified fly ash	Cr(VI)	5.9762 mg g^{-1} (From Langmuir isotherm $R^2 = 0.9888$)	Langmuir, Freundlich / N.A	(Deng et al. 2018)
Raw and mechanically activated fly ash	Cu(II)	Raw: 70.5 mg g^{-1}, Mechanically activated: 78.6 mg g^{-1}, at room temperature (obtained from kinetic studies)	Langmuir / pseudo-second order	(Xiyili et al. 2017)
Raw and mechanically activated fly ash	Mn(II)	Raw: 41.4 mg g^{-1} Mechanically activated: 48.4 mg g^{-1}, at room temperature (obtained from kinetic studies)	Langmuir / pseudo-second order	(Xiyili et al. 2017)
Raw and mechanically activated fly ash	Ni(II)	Raw: 54.3 mg g^{-1}, Mechanically activated: 73.3 mg g^{-1}, at room temperature (obtained from kinetic studies)	Langmuir / pseudo-second order	(Xiyili et al. 2017)
Raw and mechanically activated fly ash	Zn(II)	Raw: 66.0 mg g^{-1}, Mechanically activated: 80.1 mg g^{-1}, at room temperature (obtained from kinetic studies)	Langmuir / pseudo-second order	(Xiyili et al. 2017)
Thiol Functionalized Coal Fly Ash	Hg(II)	326.80 mg g^{-1} at 303 K (From Langmuir isotherm $R^2 = 0.9909$)	Langmuir / pseudo-second order	(Dash et al. 2017)
Dyes				
Rice straw fly ash	Azorhodanine	69.67 mg g^{-1} at 298 K (From Langmuir isotherm $R^2 = 0.801$)	Freundlich / pseudo-second order	(El-Sonbati et al. 2016)

Table 2 (continued)

Adsorbent	Pollutant	Maximum removal capacity	Dominant isotherm / kinetic model	Ref
Rice straw fly ash	Reactive blue 19	38.24 mg g^{-1} at 298 K (From Langmuir isotherm R^2 = 0.997)	Langmuir and Freundlich / pseudo-second order	(El-Bindary et al. 2016)
Fly ash	Malachite green	1.09 mg g^{-1}	Freundlich / pseudo-second order	(Dubey et al. 2015)
Raw coal fly ash	Methylene blue	5.06 mg g^{-1} at 298 K (From kinetic studies)	N.A / pseudo-second order	(Li et al. 2018)
Ball milled coal fly ash	Methylene blue	7.97 mg g^{-1} at 298 K (From kinetic studies)	N.A/ pseudo-second order	(Li et al. 2018)
Hydrothermally modified fly ash	Methylene blue	94.3% (pH 10, adsorbent dose of 10 g L^{-1}, contact time of 90 min, temperature 313 K)	Langmuir / pseudo-second order	(Mor et al. 2018)
Sulfonic acid functionalized heat and alkali treated coal fly ash	Malachite green	220.26 mg g^{-1} at 303 K (From Langmuir isotherm R^2 = 0.9994)	Langmuir / pseudo-second order	(Dash et al. 2018)
Sulfonic acid functionalized heat and alkali treated coal fly ash	Rhodamine 6G	358.42 mg g^{-1} at 303 K (From Langmuir isotherm R^2 = 0.9995)	Langmuir / pseudo-second order	(Dash et al. 2018)
Fly ash modified with Ca(OH)$_2$/ Na$_2$FeO$_4$	Methyl orange	14.76 mg g^{-1} (obtained from kinetic studies)	Freundlich / pseudo-second order	(Gao et al. 2015)
Polyethyleneimine- functionalized fly Ash	Malachite green	161.81 mg g^{-1} at 298 K (From Langmuir isotherm R^2 = 0.9927)	Langmuir / pseudo-second order	(Dash et al. 2016)
Polyethyleneimine- functionalized fly Ash	Reactive red 2	218.82 mg g^{-1} at 303 K (From Langmuir isotherm R^2 = 0.9979)	Langmuir / pseudo-second order	(Dash et al. 2016)
Other pollutants				
Fly ash	2,4-dichlorophenoxyacetic acid	4.05 mg g^{-1} at 298 K (From Langmuir isotherm R^2 = 0.9945)	Langmuir / pseudo-second order	(Kuśmierek & Świątkowski 2016)
Bagasse fly ash	2,4-dichlorophenoxyacetic acid	5.63 mg g^{-1} at 303 K (From Langmuir isotherm R^2 = 0.989)	Langmuir / N.A	(Deokar et al. 2016a)
Bagasse fly ash	Diuron	10.14 mg g^{-1} at 303 K (From Langmuir isotherm R^2 = 0.994)	Freundlich / Elovich and pseudo-second order	(Deokar et al. 2016b)
Fly ash	Phosphate	10.70 mg g^{-1} at 303 K (From Langmuir isotherm R^2 = 0.967)	Langmuir / pseudo-second order	(Wang et al. 2016)
Fly ash -modified by FeCl$_3$	Phosphate	71.43 mg g^{-1} at 303 K (From Langmuir isotherm R^2 = 0.963)	Langmuir / pseudo-second order	(Wang et al. 2016)
Coal fly ash	p-nitrophenol	0.775 mg g^{-1} at 303 K (obtained from kinetic studies)	N.A. / pseudo-second order	(Wang et al. 2018)
Coal fly ash activated with H$_2$SO$_4$	p-nitrophenol	1.07 mg g^{-1} at 303 K (obtained from kinetic studies)	N.A. / pseudo-second order	(Wang et al. 2018)

Fig. 2 Diagrammatic sketch of the removal of Cd(II) from aqueous solution by hydrothermally modified circulating fluidized bed fly ash. This image is reproduced with the permission from Ref. (Qiu et al. 2018)
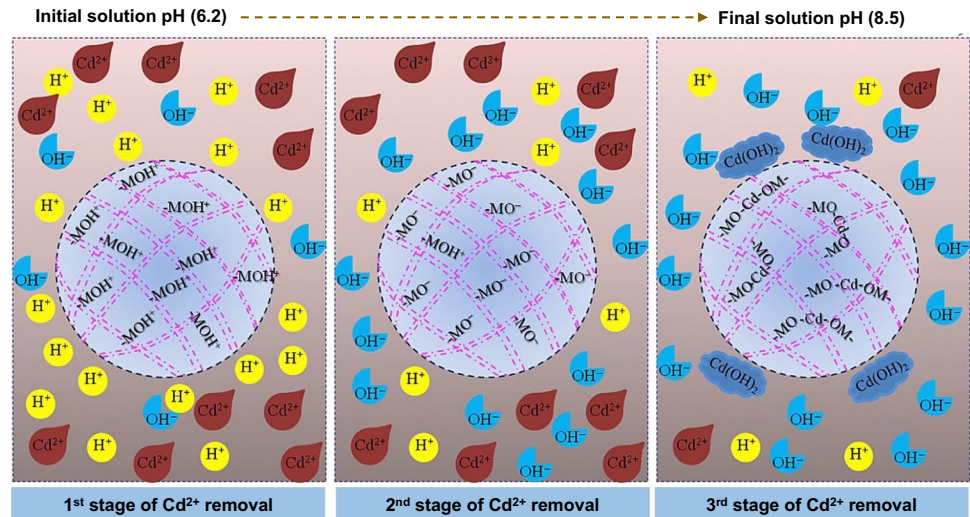
silica content and surface activity of the fly ash. The thermodynamic study proves that the adsorption was spontaneous and endothermic. Desorption tests revealed an excellent recovery of these metals that can facilitate the recycling and regeneration of spent adsorbents. For example, Cu(II) exhibited the highest desorption among the tested metal ions. After 30 min of desorption (with 0.1 M HCl), about 87% and 92% of Cu(II) was recovered for raw fly ash and activated fly ash. Similarly, the use of NaOH-treated fly ash to remove Cu(II) and Zn(II) indicated that the adsorption was spontaneous and endothermic (Sočo & Kalembkiewicz 2015). Intra-particle diffusion model suggested that the initial adsorption rate was controlled by the film diffusion, which was followed by pore diffusion or external mass transfer effects. Thiol-modified coal fly ash was synthesized and investigated for Cd(II) and Hg(II) uptake (Dash et al. 2017). The adsorption of Hg(II) was higher than the Cd(II) suggesting the higher affinity of the Hg(II) with the adsorbent. The activation energy was estimated to be 11.51 kcal mol^{-1} and 7.78 kcal mol^{-1} for Hg(II) and Cd(II), respectively, indicating the physisorption mechanism. For both metals, the adsorption process was found to be spontaneous and endothermic. During adsorption–desorption cycles, proficient stability has been noted for the used adsorbent that retained its efficiency for four consecutive cycles. Similarly, Huang et al. (2020) reported an increase in surface area and adsorption efficiency of NaOH-modified fly ash to remove Pb(II) and Cd(II). However, its removal efficiency has been affected by the antagonistic effects caused by co-existing cations as Ca(II), Mg(II), Na(I), and K(I). The reaction of metallic oxides in fly ash (SiO_2 and Al_2O_3, etc.) and NaOH introduced the cracking in dense network structures on its surface where Na^+ and OH^- were attached forming new unsaturated active bonds and ultimately improving

its efficiency (Fig. 3). Prominent adsorption mechanisms included complexation with surface functional groups, ion exchange and adsorption (Fig. 3) (Huang et al. 2020).

In addition to physico-chemical modification reported above, the efficiency of fly ash can also be enhanced by preparing its nanocomposites (Visa et al. 2015; Wang et al. 2020a). Coating nanomaterials on the surface of fly ash could improve its surface properties and more active functional groups leading to higher pollutant adsorption (Umejuru et al. 2020; Wang et al. 2020a). This would also provide a solution for the problem of nanomaterials aggregation. For example, the use of $Mg(OH)_2$/calcined fly ash nanocomposite improved the surface area (from 2.5 to 31 m^2 g^{-1}) and pollutant removal efficiency for Cu(II) (from 1 to 91%), Zn(II) (from 0.63 to 89%), and Ni(II) (from 0.4 to 88%) as compared to the raw fly ash (Wang et al. 2020a). It has been further suggested that adsorption occurred either through physical, electrostatic or chemical interactions. This prominent increase in the efficiency of nanocomposite as compared to pristine fly ash highlight the efficiency of nanocomposites. However, a better understanding of the fate and ecotoxicity of nanomaterials in environment is called for.

Fly ash-based adsorbents for the removal of dyes

Rice straw fly ash was used as an adsorbent to remove azorhodanine dye from an aqueous solution (El-Sonbati et al. 2016). The Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore volume were estimated to be 67.4 m^2 g^{-1} and 0.134 cm^3 g^{-1}, respectively. Maximum dye adsorption was observed at pH = 2 and with the rise of temperature from 298 to 333 K the adsorption was found to increase. The thermodynamic studies showed that the adsorption was spontaneous and exothermic. The activation energy (E_a) was found to be 10.89 kJ mol^{-1} indicated the
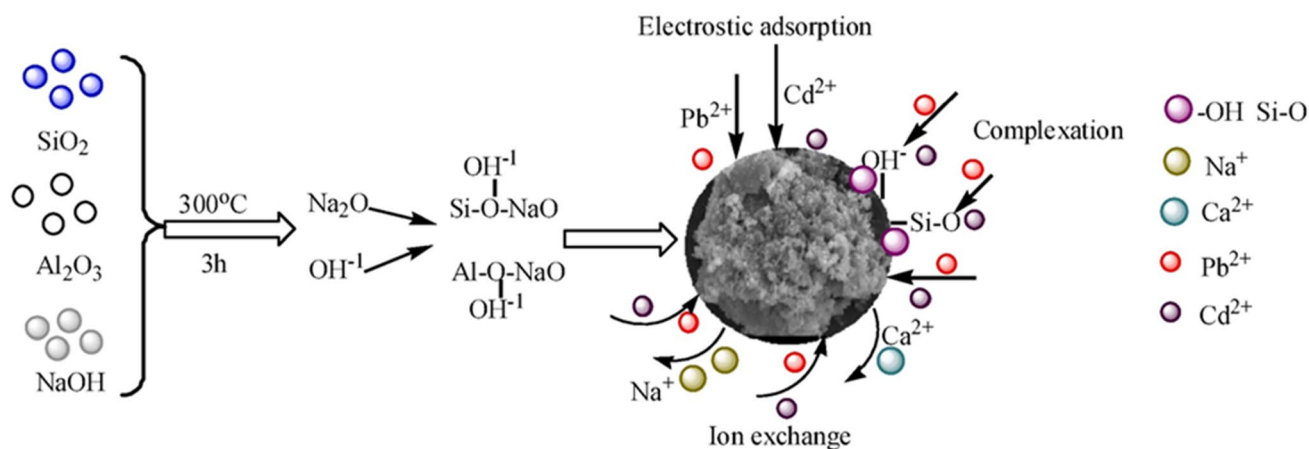
Fig. 3 The process of fly ash modification by NaOH and the proposed mechanisms of Cd(II) and Pb(II) adsorption onto NaOH-modified fly ash. This figure is reproduced with the permission from Ref. (Huang et al. 2020)

binding process occurred through physisorption. Rice straw fly ash was also applied to adsorb the reactive blue 19 dye (El-Bindary et al. 2016). The maximum removal was noticed at pH = 1 and at 60 min of contact time. The mechanism of adsorption of dye onto RSFA was physisorption as revealed by the E_a value (18.87 kJ mol^{-1}). The negative ΔG^0 and ΔH^0 values suggested the spontaneity and exothermicity or the uptake process. In another study, the adsorption of malachite green by fly ash was investigated (Dubey et al. 2015). The maximum uptake given at pH of 8 gave the equilibrium achieved in 60 min. The adsorption was found to be spontaneous and endothermic. Raw coal fly ash (Li et al. 2018), ball-milled coal fly ash (Li et al. 2018) and hydrothermally modified fly ash (Mor et al. 2018) were explored to remove methylene blue dye. The increment of pH from 2 to 12 led to an increase in the adsorption of dye (Mor et al. 2018). At equilibrium time (after 50 min), the removal percentage was 99.7% and 62.7% for ball milled fly ash and raw fly ash, respectively (Li et al. 2018). The adsorption was found to be spontaneous and exothermic (Mor et al. 2018). Another study evaluated the use of coal fly ash to remove disperse blue and disperse orange dyes (Kisku et al. 2015). The maximum removal percentage for disperse blue was estimated to be 71% (concentration 10^{-4} M, temperature 45 °C, dosage 4 g 50 mL^{-1}, pH 6) and 75% for disperse orange dye (concentration 10^{-4} M, temperature 45 °C, dosage 3 g 50 mL^{-1}, pH 6), respectively. The adsorption equilibrium data followed the Langmuir isotherm model and the kinetic data the pseudo-second-order kinetic model, respectively. The adsorption data showed that removal of dye from aqueous phase was a complex process, involving both boundary layer diffusion and intra-particle diffusion. Sulfonic acid-functionalized heat- and alkali-treated coal fly ash (HATF-SO$_3$H) was prepared and applied to remove the malachite green (MG) and rhodamine 6G (R6G) dyes from aqueous media

(Dash et al. 2018). The BET surface area, pore diameter, and pore volume were estimated to be 69.36 m^2 g^{-1}, 2.98 nm and 0.24 cm^3 g^{-1}. The highest uptake appeared at pH = 8 for both dyes (MG: 98.62% and R6G: 98.28%). The increase of temperature from 298 to 333 K was found to affect differently the removal of dyes. More specifically, the maximum removal for MG (99.19%) and R6G (98.69%) appeared at 308 K and at 313 K, respectively. The adsorption of dyes onto the adsorbent surface occurs via both electrostatic and H-bonding interactions between the surface of HATF-SO$_3$H and MG and R6G molecules (Fig. 4). Desorption experiment was performed three times and the results showed that a high amount of dyes (87.61% for R6G and 88.31% for MG) was desorbed after the third adsorption–desorption cycle indicating the high reusability of this material. Gao et al. (2015) used fly ash modified with Ca(OH)$_2$ and Na$_2$FeO$_4$ and examined its adsorptive capability for methyl orange (MO). Maximum adsorption percentage of 99.2% was obtained at the following conditions: adsorbent dose: 4.00 × 10^{-3} g mL^{-1}, initial MO concentration of 50 mg L^{-1}, pH 10, and 40 min of contact time. In another work, heat and alkali treated fly ash functionalized with PE1 (polyethyleneimine) to fabricate polyethyleneimine-functionalized fly ash and applied for malachite green and anionic reactive red 2 (RR2) (Dash et al. 2016). The thermodynamic studies revealed that the adsorption was spontaneous and endothermic with an increase of randomness at the soil/liquids interface. The adsorption of dyes onto polyethyleneimine-functionalized fly ash has been linked to several mechanisms such as H-bonding, π-π interaction and electrostatic interaction between the adsorbent and dyes. The regeneration capacity of the polyethyleneimine-functionalized fly ash was explored by three successive adsorption–desorption cycles and the estimated desorption percentage for 1st, 2nd and 3rd cycle was about to be 97%, 93%, and 89%, for MG and 95%,

Fig. 4 Adsorption mechanism for (a) Rhodamine 6G and (b) Malachite green using Sulfonic acid functionalized heat and alkali treated coal fly ash as an adsorbent. This image is reproduced with the permission from Ref. (Dash et al. 2018)
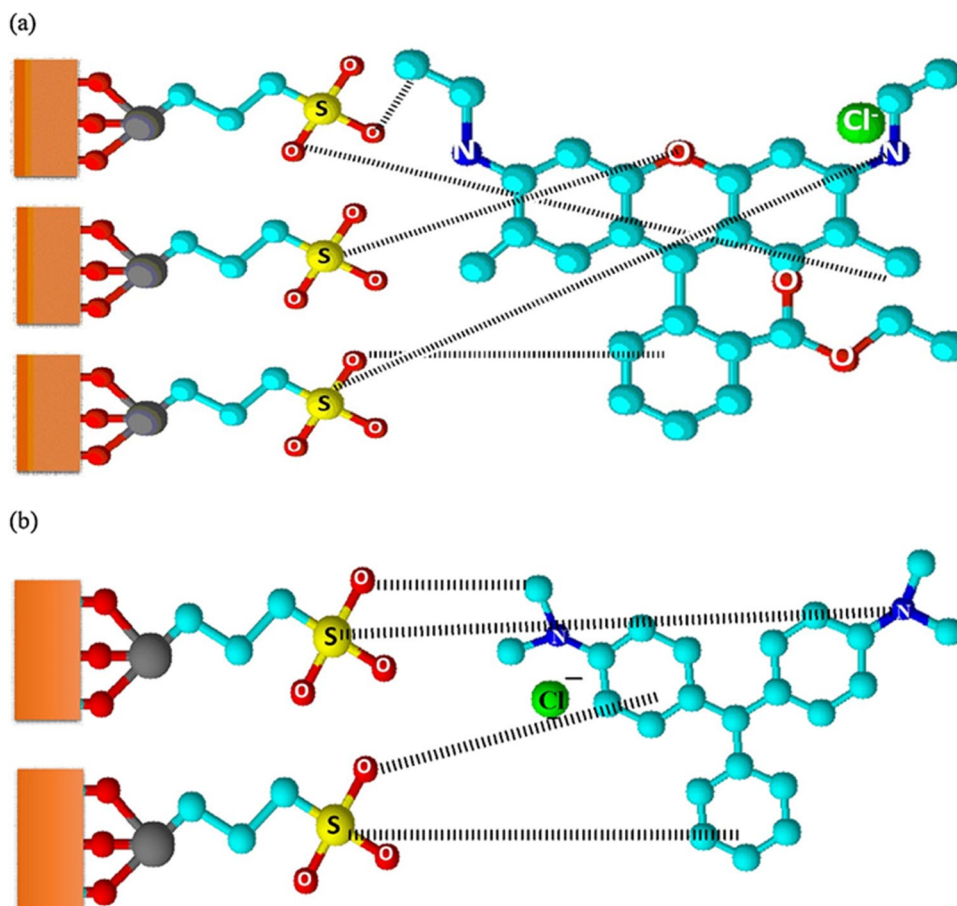
92%, and 88%, for RR2, respectively. These findings highlight the strong regeneration and reusability of the tested material.

Fly ash-based adsorbents for the removal of other major pollutants

Kuśmierek and Świątkowski (2016) examined the application of fly ash to remove 2,4-dichlorophenoxyacetic acid from an aqueous solution. The increment of pH from 2 to 12 and the presence of salt in the solution lead to a decrease in the adsorption. Kinetics studies showed that the equilibrium was attained in 60 min. The thermodynamic studies showed that the adsorption was spontaneous and endothermic. In another study, bagasse fly ash (BFA) was used to adsorb 2,4-dichlorophenoxyacetic acid (Deokar et al. 2016a). The equilibrium time was achieved in 360 min and 720 min for initial concentrations of 50 (mg L^{-1}) and 400 (mg L^{-1}), respectively. The increase in pH from 2 to 12 affected negatively the uptake. The removal process was also found as the previous study to be spontaneous and endothermic. Bagasse fly ash was also used for diuron removal (Deokar et al. 2016b). The BET surface area, micropore area, external surface area (estimated from BET surface area and micropore area), pore volume, and pore diameter calculated to be 51.93 m^2 g^{-1}, 13.67 m^2 g^{-1}, 38.26 m^2 g^{-1}, 4.96×10^{-2} cm^3 g^{-1}, and 45.577 Å, respectively. An increase in pH from 2 to 12 had a positive impact on the adsorption of diuron. The authors explained their results based on the pH$_{pzc}$ of the adsorbent (pH$_{pzc}$ = 8–9) and the species of the diuron (solution pH > 6: neutral, solution pH < 6: cationic). Based on this, at pH = 2–7, there exist electrostatic repulsive interactions between the BFA and diuron; around pH of 7, non-electrostatic interactions; and at pH > 7, non-electrostatic interactions are predominant. In a temperature range of 303 K to 328 K, the adsorption was found to be spontaneous and endothermic. Another team (Wang et al. 2016) investigated the adsorptive properties of raw and FeCl$_3$-modified fly ash for phosphate removal. The modification was found to improve the adsorption capacity of fly ash (Q$_{max}$ from Langmuir isotherm model for fly ash: 10.70 mg g^{-1}, Q$_{max}$ from Langmuir isotherm model for modified fly ash: 71.43 mg g^{-1}). Based on P fractionation, more Fe-bound P was observed because of the increment of the Fe content in the modified fly ash. Another team (Wang et al. 2018) examined the adsorptive properties of raw (RFA) and acid-activated coal fly ash (AFA) to remove *p*-nitrophenol from an aqueous solution. Optimum adsorption capacity

(1.1 mg g^{-1}) of modified coal fly ash was observed at the following preparation conditions: [H$_2$SO$_4$] = 1 mol L^{-1}, activation time = 30 min, the ratio of coal fly ash to acid = 1:20 (g:mL) and calcination temperature = 100 °C. Compared to RFA, the AFA was found to have stable adsorptive performance in a pH range from 1 to 6. The rise of temperature from to 283 K to 323 K led to a slight decrease in the adsorption capacity for both adsorbents.

To summarize, fly ash-based adsorbents were found efficient to remove various pollutants from waste(waters). Langmuir´s model was found to fit better to the experimental equilibrium adsorption data and the pseudo-second-order model well described the adsorption kinetic data. The adsorption was also found to be spontaneous and, in most cases, exothermic.

Applications of fly ash to immobilize contaminants in soils

Soil not only works as a source of nutrients to plants but also acts as a sink for pollutants that accumulate in soils causing their contamination. Soil contamination is a major environmental concern worldwide. A significant amount of recent research has focused on the development of strategies to remediate contaminated soils. Immobilization has become a prominent remediation strategy that involves the containment of pollutants in the soil to reduce their mobility, bioavailability, and ultimately the associated risks (Haris et al. 2021; Usman et al. 2020). For this, contaminated soils are amended with a variety of organic and inorganic amendments (Hamid et al. 2020, 2019). Owing to its huge

production, high availability, and rich elemental composition, fly ash has received considerable attention for soil remediation and amelioration (Buragohain et al. 2018; Xu et al. 2021). Its high surface area and strong binding capacity facilitate the contaminant fixation on its surface reducing the mobility and availability of these pollutants in soil (Huang et al. 2019; Inkham et al. 2019). Figure 5 provides a comprehensive summary of the characteristics and applications of fly ash to ameliorate metal contaminated soils.

The suitability of using fly ash has been for pollutant immobilization has been evident from many studies. For example, the application of fly ash in Eutric Fluvisols reduced the exchangeable and soluble fraction of Pb by 14% (Shaheen & Rinklebe 2015). In another pot study of 45 days, the contents of DTPA extractable Cd, Cu, and Pb were decreased by 88–94%, 74–78%, and 74–84% respectively, in a sandy loam soil with fly ash application (1–10% w/w ratio) (Mahar et al. 2016). This decrease in metal contents has been accompanied by an increase in the soil pH from 5.5 to 7 that could facilitate the immobilization of Cd and Cu by increasing precipitation and adsorption. Moreover, the increase in organic matter due to the addition of fly ash was also suggested to play its role in improved adsorption. Despite this decrease in DTPA extractable metal contents, the concentration of these metals increased in the Chinese cabbage plant biomass. This has been attributed to the formation of Cd carbonate fraction during the immobilization process which gets dissolved in the rhizosphere (Mahar et al. 2016). In an inceptisol soil, the binding of Cu and Zn was increased by 61 and 113%, respectively, that has been linked to an increase in carbonate bound and exchangeable fractions by fly ash (Lee et al. 2019). They, however, reported that fly ash may

Fig. 5 Characteristics, environmental risks, and potential applications of fly ash for metals amelioration in soils
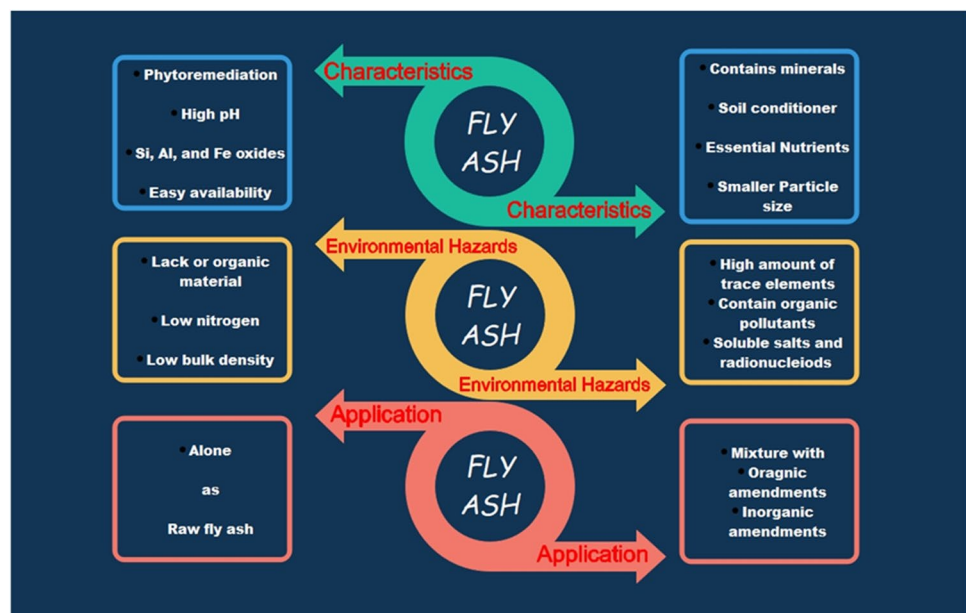
also adsorb the nutrients due to its non-selective nature and, thus, co-decrease their availability with toxic elements by sorption and precipitation. Therefore, the immobilization of toxic metals as well as nutrients should be considered. The effects of the fly ash amendment on soil health and quality are discussed in the next sections (Sect. 4.1). A two-year trial in a paddy field also reported that the addition of fly ash decreased the availability of Cd from 1.26 to 1.10 mg kg^{-1} (Zhao et al. 2020).

The effect of soil type was highlighted by Wang et al. (2020b) on cadmium mobility in three different soils amended with fly ash. Their data revealed a substantial decrease of 18–52% in the DTPA extractable Cd in sandy soil, followed by a 5.9 ~ 16.7% reduction in yellow–brown soil and a negligible impact in clayey soil. Therefore, the efficiency of fly ash is dictated by the soil type. In another study with two clay loam soils, the application of corn-cob fly ash (1.86 g g^{-1} of soil) was unable to reduce the exchangeable and reducible Cd probably due to its poor efficiency (Inkham et al. 2019). Rather, DTPA-extractable metal concentration slightly increased (from 29 to 32 mg kg^{-1}) with the addition of fly ash due to its high inherent Cd contents (5.7 mg g^{-1}). Similarly, the addition of fly ash at a higher dose (100% on soil volume basis) increased the DTPA extractable metal contents (e.g. from 0.8 to 1.89 for Pb, 0.06 to 0.28 for Cd, from 0.78 to 2.65 for Cu). It has been linked to the alkaline pH (7.7) and high inherent metal contents of fly ash (e.g. Pb = 2.44 mg kg^{-1}, Cd: 0.43 mg kg^{-1}, 4.5 mg kg^{-1}) (Nayak et al. 2015). They further supported that the application of highly alkaline fly ash to acidic soil could decrease the trace metals' release whereas in an alkaline soil, the release of these elements remained unchanged. These findings highlight the role of soil type and fly ash nature in dictating the efficiency of fly ash in pollutant immobilization. As discussed in Sect. 2, fly ash is characterized by different physicochemical properties and structural compositions. The abundance of negatively charged hydroxyl groups could bind metallic cations (Dai et al. 2018). The adsorption peaks also indicate the presence of calcite groups which could be attributed to the stretching of O-C-O bands. Moreover, the presence of other groups such as Si–O–Si and Al–O–Si might also be responsible for enhanced metals adsorption (Huang et al. 2019). The complex structure and heterogeneous morphology of applied fly ash are also evident from other studies. For example, SEM analysis revealed the existence of fly ash in a spherical amorphous structure with needle-like shape having a range of particle size between 10 and 50 μm (Bidar et al. 2016). Similarly, fly ash generated by a waste power generation plant showed the presence of flocculent and laminar structures instead of crystalline structures (Huang et al. 2019). The elemental analysis carried out with EDX detected the various elements (Al, Si, O, S, C, P, K, Se, Pb, and Ti). The mineral components of fly ash can release

anionic compounds leading to the binding of cationic components. The above discussion concludes that the functional groups, mineral states, and structural differences have direct influence on the fate of metals in the contaminated environment. Therefore, the quantity, as well as quality of fly ash, should be thoroughly studied to evaluate its suitability for a particular soil.

To further improve the efficiency of fly ash, various strategies have been proposed that include its pretreatment or its application in composite with other amendments. Alkaline pretreatment of fly ash improves the metal stabilization by decreasing the metals' solubility (through precipitation) and their exchangeable contents in soil (He et al. 2017). The alkaline pH could also facilitate metal-carbonate precipitation and oxide formation. Moreover, its role in dictating the soil's pH also dictates the solubility and dissolution of several other mineral phases that further impact the transfer of metals (Brännvall et al. 2015).

The efficiency of fly ash can also be improved by its application as composites with other inorganic or organic amendments. The co-application of fly ash with organic amendments, especially with animal or poultry manure and sewage sludge, has been found to enhance nutrient availability and reduce metal solubility further decreasing metal contents in plant parts (Munir et al. 2020). Also, the combination of biochar and fly ash significantly reduced the metals availability and subsequent accumulation in maize. The bioavailable fraction of Cu and Cr were significantly reduced between 44–53% and 47–66% respectively. Mixing biochar with fly ash leads to the establishment of several mechanisms like precipitation, complexation, or adsorption due to the increment in binding sites (Yin et al. 2017). Similarly, the composites of hybrid fly ash and animal-derived biochar improved the soil pH and significantly reduced the CaCl$_2$ and TCLP extractable Cd by 91 and 70% respectively. This combined treatment also reduced Cd accumulation in rice grains (Lei et al. 2020). In another study, the stabilization of Cd, Zn, Fe, and Cu was achieved in soil and fly ash mixture by the application of deionized and acidic water. The results revealed that acidifying the material leads to the leaching of toxic elements as compared to deionized water application. The results of this study also suggest fly ash as a sustainable material to mitigate the leaching of toxic metals (Kankaraju et al. 2019) and nutrients (Lim et al. 2016) in groundwater. In a recent study (Yu et al. 2022), a composite amendment of rice straw biochar, fly ash, and white marble modified through oxidization significantly reduced the Cd bioavailability in soil by 10–26% along with an increase in soil pH. The application of this composite amendment decreased Cd concentration in brown rice by 40.49 and 41.59% in pot and field experiment, respectively (Yu et al. 2022). However, the composite samples may exhibit negative metal retention and poor rice growth as observed when fly ash and zeolite

were applied together (Lim et al. 2016). It should be noted that zeolite, an efficient environmental material, can be synthesized from fly ash (Qiu et al. 2018). The synthesis of new materials from raw fly ash can solve the potential impacts of environmental pollutants. For example, Qiu et al. (2018) synthesized the zeolite from fly ash and reported the reduced environmental risks of trace metals and improved the resource utilization of solid wastes. Previously, Ghrair et al. (2010) also confirmed the fly ash synthetic zeolite-based alleviation of metals toxicity to plants and reduction in contaminants bioavailability in soil. Fly ash can also be converted to zeolite and other intermediate materials through low-temperature alkali roasting. Their application significantly decreased the available Cd contents by 26.9 and 26.0%, respectively in a two year field study of contaminated paddy soil (Zhao et al. 2020). The conversion of fly ash into zeolite or other materials are not the focus of this review. Similarly, the use of fly ash enabled the coupling of metal stabilization with advanced oxidation processes (Ma et al. 2018). The advanced oxidation processes show great potential to remediate contaminated environments (Usman et al. 2018b, 2022; Usman & Ho 2020) but, they are beyond the focus of this review.

Implications of fly ash in soil–plant system

The application of fly ash in soil systems has considerable impacts on soil health and plant growth. The impacts of fly ash on soil's physico-chemical characteristics, microbial activity, soil fertility, and plant growth are described in the following sections.

Impacts of fly ash on the physico-chemical characteristics of soil

A high concentration of nutrients in soil may not be of agricultural importance if soil characteristics are not favorable for its uptake by plants. As elaborated in Sect. 2, fly ash contains small particles of silt or clay and has low bulk density, high volume stability, high water holding capacity, alkaline pH. All these features make it a potential ameliorant for soils with a strong ability to alter the soil's physical properties (Xu & Shi 2018). The application of fly ash in soil with poor physical characteristics alters the bulk density, texture, and water holding capacity of the soil. The amendment of coarse-textured soils with fly ash results in the improvement of silt/sand-sized particles ultimately helping in improving soil water storage, infiltration, and aggregation (Skousen et al. 2013).

The degree of changes in the physical properties of soil depends upon three main factors i.e. soil type, the nature of fly ash and the amount of fly ash. For example, alkaline fly

ash can be used to ameliorate the acidic soils which helps in reducing the mobility and availability of toxic metals in acidic contaminated soils (Saraswat & Chaudhary 2014). Similarly, the application of fly ash especially in higher amounts (~ 70 t ha^{-1}) can even induce the development of finer soils by temporarily manipulating the soil texture (Sahu et al. 2017). Fly ash enhances the soil micro-porosity that improves the water holding capacity and soil bulk density and reduces soil compaction. All these factors significantly improve nutrient uptake in plants (Sahu et al. 2017). The fly ash particles (hollow sphere-sized) can replace the bigger soil particles and accumulate in soil voids ultimately modifying the soil texture and porosity (Ram et al. 2007). The highly soluble Ca fractions in fly ash and a high percentage of particles of different sizes (2–200 μm) can also improve the soil structure (Yunusa et al. 2006). Amending soil with fly ash alters the soil texture from sandy clay to sandy clay loam and from sandy loam to silty loam where the fly ash addition also increased the water holding capacity of sandy soil and/or sandy loam soil (Jambhulkar et al. 2018). In rainfed agriculture and sandy soils, the response was more evident on water holding capacity and nutrient retention in the soil. However, the application of fly ash did not improve soil bulk density when both the soil and fly ash have the same density (2.16 g cm^{-1}) (Adriano & Weber 2001). It should be noted that despite this negligible impact on soil bulk density, the use of fly ash improved the water holding capacity of soil and available water contents for plants. This has been linked to the large surface area of fly ash particles that increase the soil microporosity and ultimately the water holding capacity (Adriano & Weber 2001). Similar results were presented elsewhere (Pandey & Singh 2010) that the usage of fly ash tends to decrease bulk density and improve water holding capacity. Moreover, it is worthy to note that the improvement in the water holding capacity and plant available water content were achieved mostly at high application rate of fly ash (560 and 1120 t ha^{-1}). However, the high application rate of fly ash might also induce some undesirable effects on soil quality and metal contents as discussed in Sect. 4 (Jambhulkar et al. 2018).

Fly ash, due to its liming potential, can also contribute to reclaiming sodic and contaminated soils (Inkham et al. 2019; Kankaraju et al. 2019). These authors further reported that the changes in the chemical properties of the soil also depend upon the chemical properties of fly ash. The pH value of fly ash lies between 1.2 and 12.5 with most ashes showing alkaline pH. Based on the pH value, the fly ash is mostly divided into highly acidic, moderately alkaline (pH: 8–9), and strongly alkaline (pH: 11–13) (Yao et al. 2015). The application of fly ash is most likely to be used for improving the soil pH, but the degree of changes in soil pH depends upon several factors e.g. pH of fly ash, soil buffering capacity, and neutralizing capacity of fly ash due to

the presence of MgO and CaO contents (Yao et al. 2015). The application of acidic and alkaline ashes (F class) to clay loam and acidic sandy clay soils presents the low efficiency of ashes in ameliorating the soil pH. However, the ash with high calcium carbonate contents raised the soil pH by more than 2 units (Manoharan et al. 2010) which plays a tremendous role in bringing vast area of non-productive lands to productive area (Yao et al. 2015). At high pH, the dominance of Si, Ca, Fe, and Al oxides or hydroxides forms various secondary minerals or chemicals that bind the metals improving their immobilization (Belviso et al. 2015). The sulfo-, silica- and alumino- oxides containing fly ash facilitated the buffering of the acidic pH in contaminated soils and limited the mobility and availability of trace metals (Nayak et al. 2015). Silicate minerals, which exist in substantial amounts in fly ash, take up cation (H^+) and neutralize the soil pH. Moreover, this fly ash-induced increase in soil pH improves the immobilization of toxic elements as pH is considered the main determining factor in regulating the fate of toxic metals (Bidar et al. 2016). The increase of pH and HCO_3^- with the application of alkaline fly ash has also been linked to the dissolution of $CaCO_3$ and CaO with formation of bicarbonate around circumneutral or alkaline pH values (Jankowski et al. 2006). Therefore, fly ash can be a good option for the reclamation of mine soils and revegetation of such degraded soils with low fertility and high compaction and bulk density. The high pH of fly ash makes it an attractive substitute to lime for the reclamation of acidic soils (Fernández-Delgado Juárez et al. 2020).

Impacts of fly ash on soil microbial activity

Higher microbial activity in the soil is strongly linked to nutrient availability in all types of soils. Various strategies are used to augment soil fertility through microbial interventions such as the inclusion of organic matter mineralization microbes, mycorrhizal association, nitrogen-fixing rhizobia, etc. (Jacoby et al. 2017). The addition of soil organic matter to soil enhances the microbial activity in most agricultural lands. However, studies evaluating the impact of fly ash on soil microbial activity are relatively limited.

Generally, enzyme activity is recognized as a good indicator of soil quality because of the role of enzymes in soil biological processes and their quick response to soil changes (Nayak et al. 2015). Fly ash, even at 10% w/w dose, had a positive impact on the activity of intracellular enzymes in a mine soil. The activities of dehydrogenase and alkaline phosphatase were increased up to 536% and 48%, respectively (Álvarez-Ayuso & Abad-Valle 2021). An increase in the growth of fungi including arbuscular mycorrhizal fungi and gram-negative bacteria has been witnessed after the application of fly ash to soil at a rate of 505 tons ha^{-1} (Schutter & Fuhrmann 2001).

However, excessive levels of coal fly ash inhibit the enzymes activities and nitrogen cycling processes such as nitrification and mineralization in coarse-textured soils due to high contents of salts and toxic metals (Pandey & Singh 2010). It has been reported elsewhere that lower doses of fly ash (up to 40% on soil volume basis) may improve the micronutrient availability and microbial activity. However, a further increase in the dose of fly ash suppressed the microbial activity and growth due to the higher accumulation of toxic metals in soils (Nayak et al. 2015). They further reported that the addition of fly ash up to 40% on soil volume basis does not interfere with the N mineralization process in heavy textured soil due to an improved aeration. Moreover, microbes responded differently to the dose of fly ash. The population of both actinomycetes and fungi were decreased with the addition of fly ash in soil, while aerobic heterotrophic bacterial population did not change significantly up to the dose of 40% (Nayak et al. 2015). A recent study reported that the application of fly ash (6% on soil volume basis) did not affect the soil basal respiration and urease activity (Leclercq-Dransart et al. 2019). However, fungal activity was enhanced by this amendment. Interestingly, the beneficial effect of fly ash was still evident after 14 years of the amendment. Similarly, an increase in carbon, microbial biomass, enzymatic activities, and the microbial population was noted up to 90 days after sowing of seeds (Usmani et al. 2019). All these studies highlight that the amount of fly ash should be adjusted according to its impacts on soil biological processes and microbial activity.

Use of fly ash to improve soil fertility and crop productivity

Plants require fourteen mineral elements which must be provided from the soil in required amounts for optimal plant production. But, soil cannot continue to act as a source of these elements for an indefinite time period. Since the start of agricultural production, organic manures are being used as the traditional source of nutrients in soils. However, elevated food demand has led to the development of high-yielding cultivars which generally require more nutrients. Therefore, intensive crop production has exhausted the soils of nutrients. After the green revolution, modern synthetic fertilizers contributed tremendously to producing enough food for an ever-increasing population. However, an increased dependence on commercial fertilizers has decreased the use of organic manures. This trend has deteriorated soil health reducing its overall potential. To address this, the provision of nutrients from an organic source can enhance soil health and agricultural sustainability. In this scenario, fly ash has received significant attention as an organic amendment for soils.

Fly ash is a rich source of nutrients and has the potential to be used as fertilizer. Fly ash amended soils have shown an enhanced nutrient supply and improved soil characteristics for sustainable crop production (Fig. 6). Although used in patches in various regions, it has not been included in any fertilizer recommendation plan. Indeed, its use in agriculture is very limited compared to the other organic amendments. Recent agricultural scenarios considering the deteriorating effects of climate change on soil health and over-exploitation of soils for higher food production require healthier and sustainable soils (Shahzad et al. 2019). Beneficial effects of fly ash and increasing fly ash production demand its use as a fertilizer for nutrient supply and soil health improvement. Provided below is a brief description of its role in improving soil fertility and crop productivity.
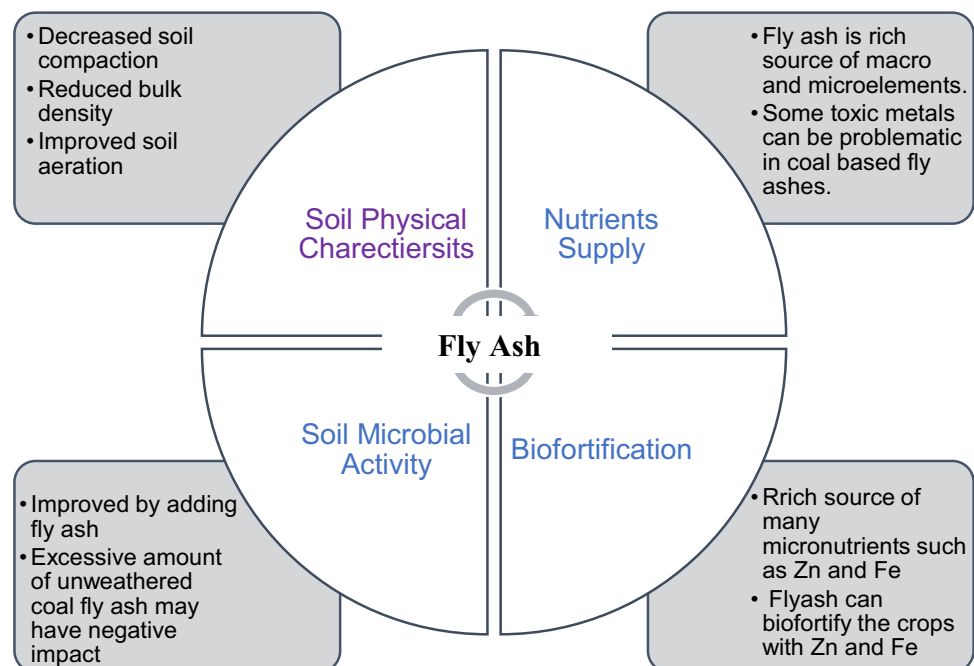
Nutrient Supply by fly ash

Mostly fly ash is a byproduct of coal or biomass burning. Both of these sources of fly ash are rich in nutrient elements, but their compositions are extremely variable. In coal fly ash, the elemental concentration is dependent on the nature of the parent material. Coal contains macro-nutrients such as P, K, Ca, Mg, and S and micronutrients including Fe, Mn, Zn, Cu, Co, B, and Mo which remain plant-available after combustion in significant amounts in the formed fly ash. However, a wide range of pH of fly ash (4.5. to 12.0) may affect the nutrient availability (Basu et al. 2009). Micronutrients are required in smaller amounts by plants. But, fly ash main contain certain micronutrients in high concentrations, such as B, that maybe toxic for plants.

The nature of fly ash produced from biomass varies due to nature of crop/plant species combusted, soil type, and soil amendments used to produce that biomass. Biomass fly ash has a relatively high concentration of essential plant elements with a low concentration of toxic metals. Plants having high nutrient requirements and/or fertilizer application determine the nutrient concentration in fly ash of those crops' biomass. A comparison between elemental concentrations in different crop species highlighted the highly variable contents of elements in fly ash (Xing et al. 2016). The range of elemental concentration has been presented in Table 3, to have an overview of elemental variation between biomass fly ash. Among macronutrients, K is greatly important from an agricultural point of view due to its deficiency in soils and the high cost of commercial chemical fertilizers available in the market (Wakeel & Magen 2017). The K concentration in biomass fly ash up to 44% K_2O has been reported (Table 3) which makes it a potential potassic fertilizer comparable to the market-available KCl, K_2SO_4, and polyhalite with 60%, 50%, and 14.5% K_2O, respectively. The biomass fly ash has an adequate concentration of all micronutrients required for plant growth and yield improvement (Quirantes et al. 2016).

Being an organic source of nutrients, fly ash has also a great potential for organic agriculture. All the micronutrients are not applied to agricultural land in general practices. The application of fly ash promotes nutrient cycling and soil sustainability. Both coal, as well as biomass ashes, are a rich source of most essential mineral elements required by plants and their application to soil have promising effects on soil fertility and crop growth (Basu et al. 2009; Shakeel et al. 2019), However, high concentration of toxic metals

Fig. 6 Four major impacts of fly ash application to soil contributing soil fertility and crop productivity

- Decreased soil compaction
- Reduced bulk density
- Improved soil aeration

- Fly ash is rich source of macro and microelements.
- Some toxic metals can be problematic in coal based fly ashes.

Soil Physical Charectiersits

Nutrients Supply

Fly Ash

Soil Microbial Activity

Biofortification

- Improved by adding fly ash
- Excessive amount of unweathered coal fly ash may have negative impact

- Rrich source of many micronutrients such as Zn and Fe
- Flyash can biofortify the crops with Zn and Fe

(including essential micronutrients for plants), in coal ash must be taken into account while using for agricultural purpose. Biomass fly ash has mostly micronutrients (especially toxic metals) in safe limits and can be used without any toxicity hazards (Basu et al. 2009). However, halophytic plants biomass used in fly ash production may have a high concentration of Na as well which could negatively affect the crop productivity (Fuller et al. 2018). This point should be taken into account while using fly ash in the agricultural production systems.

Impacts of fly ash on plant growth

The influence of fly ash on soil physical, chemical, and biological activities has considerable impacts on plant development and growth (Shaheen et al. 2014). Researchers have demonstrated the positive effect of fly ash application on plant productivity and harvest (Skousen et al. 2013). Soil amendments considerably increased the dry biomass of Chinese cabbage with the application of fly ash (4 g pot^{-1}) as compared to the control (1.4 g pot^{-1}). This increment in plant biomass was attributed to the changes in soil pH from acidic (pH = 5.5) to slightly neutral (pH = 6.9) with fly ash amendment (Mahar et al. 2016). In another study, He et al. (2017) reported a significant increase in dry biomass of alfalfa shoots by 1.2–14.6 times, 2.4–17.9 times, and 1.1–17.7 times in in a loessial soil amended by the 5%, 10%, and 20% (weight ratio) of coal fly ash, respectively. However, shoot dry mass was markedly declined (by 45%) with the application of 40% treatment in the first harvest. Therefore, 5% of application rate has been suggested safe by the authors in a loessial

Table 3 Range of elemental concentration in biomass fly ash from different plant materials (Willow pellet, Rape straw, Mixed forestry pellets, White wood pellet, Miscanthus Pine, SRC willow, Olive residue, Wheat straw, Oatmeal, Peanut, Wood, Chipped wood, Straw, Torrefied wood, Wheat straw pellet). The values show concentration in wt. % and the analysis was carried out by X-ray fluorescence spectrometer and obtained data is derived from Ref. (Xing et al. 2016)

Elements	Minimum Concentration (wt. %)	Maximum Concentration (wt. %)
Na$_2$O	0.234	2.485
MgO	1.021	5.896
Al$_2$O$_3$	0.138	4.476
SiO$_2$	2.496	46.659
P$_2$O$_5$	1.494	9.742
K$_2$O	4.449	33.034
CaO	1.775	51.142
TiO$_2$	0.464	0.912
MnO	0.002	4.062
Fe$_2$O$_3$	0.239	3.401

soil. Similarly, the fly ash improved the growth yield of mustard by the application of up to 30% w/w of fly ash, whereas further increment in fly ash application reduced the growth, probably due to possible toxic effects of toxic metals (Shakeel et al. 2019). Recently, Zhao et al. (2020) conducted a two-year experiment to remediate a Cd-polluted rice field by applying raw fly ash and two new products, an intermediate product and zeolite, formed by modifying fly ash. It was revealed that the use of these amendments promoted the development and yield of rice in Cd-contaminated field. Both products improved the grain weight and rice yield by (11–12% and 29–36% as compared to the control). This improvement in yield parameters has been attributed to higher availability of nutrients and lower bioavailability of Cd (by 26% in first year and by 22–28% in the second year).

Similar improvement in the growth and yield with the application of fly ash has also been reported for other plants like maize (Masto et al. 2013), rice (Lee et al. 2006), and *Solanum melongena* (Gond et al. 2013). However, the application of fly ash presents varying effects on plant growth and trace metals mobility, and immobilization in soils. Therefore, to further improve its efficiency, mixing it with other additives or modifying the raw fly ash may yield better effects. Lei et al. (2020) stated an elevation in plant height with the application of novel ash-biochar composite (A/B biocomposite). A significant increase in plant height of early (94.6 to 97.9 cm) and late rice (100.0 to 107.8 cm) was observed with T10 treatment where 10 kg m^{-2} novel A/B biocomposite was employed. This increase in plant height might be correlated to Si that might promote plant growth. Similarly, substantial increase in the above- and below-ground biomass (475 and 156 g) of giant reed was attained with a combined treatment of fly ash and organic complex fertilizer due to a prominent decrease in available metal contents. The results showed a significant association between biomass and contamination level of soil and planting density (p < 0.05) (Liu et al. 2017).

However, contradictory results were also reported that fly ash treatment may reduce rice growth due to the negative impacts of fly ash on nutrient immobilization caused by their co-binding with toxic metals (Lee et al. 2019). In a less fertile soil, the addition of fly ash improved N and P contents by increasing their retention in soil. However, reduced mobility of these nutrients hampered rice growth (Lim et al. 2016). Large spills of fly ash can be particularly harmful to the soil (Awoyemi et al. 2019). For instance, ≥ 0.5 g m^{-2} day^{-1} coal fly ash significantly influenced all growth and yield parameters causing a significant decline in the grain yield (Raja et al. 2014). Our review mainly concerns the use of fly ash as soil amendments. Even though, it is cautioned that the application of fly ash is not always beneficial to plants. The quantity of fly ash should be tuned according to the site-specific

conditions. It is also crucial to evaluate the properties of fly ash as well as of the target soil to have optimized efficiency.

Trace elements and biofortification potential of fly ash

Intensive use of agricultural land, high-yielding cereals with low density of micronutrients, and climatic changes have reduced the national value of agricultural produce. About 820 million people are globally undernourished and about 50% global population is suffering from the deficiency of one or more micronutrients (GNR 2020). The conventional strategies to eliminate malnourishment include nutrient supplements and food fortification. However, biofortification, enriching the edible parts of food produce with micronutrients, is a relatively new strategy with significant global impact. Fly ashes are a rich source of trace elements some of which are essential elements for plants, humans, and animals and their continuous supply in the food chain is necessary for optimum human and animal health. The use of fly ash as a fertilizer has great potential for the biofortification of food crops due to high concentration of Zn, Fe, and Se. However, high concentration of some toxic metals such as Ni, Cu, As, Cr, etc. limits the application of coal ash (Basu et al. 2009). On the other hand, biomass ash generally has less concentration of toxic metals and is more appropriate for biofortification of essential elements. For example, He et al. (2019) reported that owing to its high selenium (Se) contents, fly ash can be used as a promising soil amendment for Se biofortification to address the Se-deficiency issues in a large population worldwide.

Conclusions and perspectives

Fly ash is among the major anthropogenic wastes. It is characterized by very complex composition and highly variable properties. Its physicochemical characteristics, availability in massive amounts, and good decontamination efficiency make it a viable adsorbent for the removal of pollutants from water and soil and reducing the associated risks. The properties and efficiency of fly ash can be tuned by its pretreatment (for example alkali activation) or its application with other efficient materials in composites. A better understanding of the adsorption mechanism is required considering the limited amount of information on it. We acknowledge that proposing the adsorption mechanism is a challenging task. For this, the use of sophisticated spectroscopic methods in combination with the correct interpretation of kinetic modeling would be highly rewarding. The application of composite materials combines their benefits while addressing the limitations of individual counterparts. Though nanocomposites of fly ash showed great stability and adsorption efficiency, there exists limited data on this topic. Further investigations

on the development of nanocomposites should also focus on their fate and ecotoxicity in the environment. Magnetic nanocomposites of fly ash can be particularly interesting to facilitate the recovery of spent adsorbent after wastewater treatment. It serves as a cost-effective solution for wastewater treatment, but the disposal of spent fly ash can be highly challenging considering the huge contaminant load after adsorption.

In addition to its adsorption potential in contaminated soils, the basic nature of fly ash makes it particularly useful for acidic soils where its use improves the soil pH and leads to the precipitation of toxic metals reducing their availability. It also contains a variety of beneficial nutrients and, therefore, it has been widely used as a soil amendment to improve soil fertility and plant growth. Moreover, its use also improves the soil's physical properties (soil structure, soil porosity, soil aggregation, water holding capacity, bulk density). The amount and properties of fly ash strongly affect the microbial population and activity in soils. Fly ash may also contain potentially toxic contaminants (metals, PAHs, etc.) which could have harmful impacts on soil health and plant growth especially at higher amounts of this amendment. Moreover, these contaminants may also contaminate the groundwater by leaching. These risks are particularly important at higher doses of fly ash. Therefore, the dose of fly ash should be adjusted according to its impacts on soil health and plant growth. This calls for extensive field trials considering the nature of fly ash and soil type. It would be highly rewarding to study the bioavailability of these toxic metals and the long-term impacts of fly ash addition on soil health. To summarize, the use of fly ash in wastewater treatment and soil offers a viable strategy to recycle this industrial waste but its use may pose certain risks depending upon its composition. Therefore, it should be applied with caution after thorough investigations in the soil–plant system. The application of fly ash in appropriate amounts based on site-specific conditions can mitigate the potential risks associated with its application and can promote its sustainable use.

Data availability All data generated or analyzed during this study are included in this published article.

Code availability Not applicable.

Declarations

Ethics approval and consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests Authors declare no competing interests.

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