

Removal techniques for heavy metals from fly ash

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Abstract This study reviews different technologies for extraction of heavy metals from fly ash. With this perspective processes like bioleaching using microbes, carrier in pulp method, chemical extraction via acids, alkaline leachates and chelating agents, chloride evaporation process, electro-dialytic and thermal treatments were studied thoroughly. A comprehensive comparison of all the techniques is also done by studying in detail their reaction conditions, metals leached and percentage extraction achieved. The study concluded that depending on the type of fly ash and metal under consideration determines the suitability of the process adopted for detoxification of fly ash. In addition to these, factors like cost, time and energy also define the final selection process.

Keywords Fly ash treatment · Metal extraction · Leaching characteristics · Metal concentration

Introduction

Fly ash is the major combustion residue of different processes like municipal solid waste incineration, coal burning, etc. [1] which is produced in massive amounts as a waste material. According to American Coal Ash Association (ACAA), the total amount of fly ash produced in 2013 is

53.40 million tons out of which only 23.32 million tons were used. Hence, the total consumption accounts only to 43.67% and the rest is being dumped in landfills or open lands, causing severe financial and environmental problems [2, 3].

Fly ash is composed of fine-grained particles having variable morphology [4, 5]. The major part of fly ash consisted of (1) inorganic portion which includes amorphous (glassy) and crystalline matter. Other minor constituents include (2) organic matter which is composed of char material and organic minerals and (3) fluid portion comprising moisture, gas and gas–liquid phases that might also have inorganic and inorganic constituents in them [1]. Fly ash is generally classified according to ASTM C-618, as C-type and F-type based on the amount of the primary components present, which are silica, alumina and iron oxides with ashes 50–70% and >70%, respectively [6, 7]. Several other approaches were also researched to characterize fly ash based on different parameters like availability of glassy phases [6], origin, phase, behaviour, composition, properties [1], particle size [8], etc. Some famous classification systems in use are based on (1) SiO₂/Al₂O₃ ratio, CaO and SO₃ percentage categorizing fly ash into Group I, II, III and IV. (2) Granulometry and Baline-specific surface area that group fly ash into fine, medium and coarse grained. (3) Free CaO contents with classification as inactive, active and very active. (4) Contents of SiO₂, Al₂O₃, TiO₂, Fe₂O₃, SO₃ or Fe₂O₃, MnO, SO₃, P₂O₅; CaO, MgO, Na₂O, K₂O; pH of leachate and particle size distribution when taken as classification parameters resulted in 7 classes (Sialic, Modic, Fersic, Calsialic, Feric, Fercalsic and Calcic) [1].

Thus, in addition to the primary inorganic components (Al₂O₃, SiO₂, Fe₂O₃) and other minor constituents like carbon, calcium, magnesium, sulphur, sodium, and potassium [7] that form the basis of fly ash classification, a considerable amount of heavy metals like arsenic, chromium, lead,

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mercury, etc. is also present in it [9–11] that can account for 2000–20,000 mg kg⁻¹ [12]. Another major type of fly ash is produced in addition to coal one in municipal solid waste incinerator (MSWI) fly ash, though the process of its formation is different resulting in small variations in the composition but with similar properties [13, 14]. Thus, the mineral composition of fly ash depends on the relevant composition in feed materials and may consist of alumino-silicates, oxides, sulphides, etc. [15–18]. These elements being the leachable component often leach out of the disposed fly ash waste and accumulate into sediments and soils, thereby degrading the soil quality and aggravating the air and water pollution [4, 19] which led to serious health hazards. Dust containing fly ashes result in allergic reactions and harm the natural ecology, particularly flora by blocking their stomatal openings and consequently hindering photosynthesis. Hence, there is a need to treat fly ash before its disposal, but in the majority of cases this results in the production of additional waste streams [20, 21].

So, enhancement in utilization rate of fly ash becomes the matter of primary concern, but this requires removal of heavy metals prior to utilization [7, 22–27] through endorsing suitable technologies for their ultimate safe disposal/utilization [28–32]. Also with the exhaustion of natural mineral resources, there is a need to extract, recover and reclaim these metals from the waste produced [33]. Hence, this review article focuses on the different approaches according to the nature of the processes used for the removal and recovery of heavy metals from different types of fly ash. Generally, all these processes are based on two-step methodology, i.e. removal of heavy metals followed by their collection or recovery [34].

Heavy metal removal techniques

There are many techniques researched and practiced for the removal of heavy metals, but the ones that are most promisingly used include biological processes which make use of bacteria or fungi; chemical leaching using organic acids, inorganic acids, alkaline lixivants and chelating agents; electroplating processes making use of ac/dc current setups and thermal processes consisting of combustion, smelting and amalgamation techniques. A comprehensive comparison of these techniques is discussed below and a detailed overview is given in Tables 1, 2, 3 and 4.

Biological processes

Biological processes involve several techniques amongst which bioleaching (BL) has been successful so far to remove heavy metals from fly ash owing to its less resource demanding and green nature [12, 35]. The process involves microbial conversion of solid compounds into soluble form,

making their extraction and recovery easy [35]. Many microorganisms (MO) are known to facilitate the BL of metals from solid materials [35–38] by the formation of organic and inorganic acids as by-products, such as acid, citric acid (CA), gluconic acid (GA), H₂SO₄ [35] but in case of fly ash the MO that is mostly used by researchers is fungus *Aspergillus niger* [12, 39–41]. Few other microbes that were explored include *Acidithiobacillus* [41–43], *Pseudomonas* spp. [36, 43], *Thiobacillus ferrooxidans* [36, 38] and *Thiobacillus thiooxidans* [36, 38, 44]. All these microbes belong to three main groups, i.e. (1) autotrophic bacteria (e.g. *Thiobacilli* spp.), (2) heterotrophic bacteria (e.g. *Pseudomonas* spp., *Bacillus* spp.) and (3) heterotrophic fungi (e.g. *Aspergillus* spp., *Penicillium* spp.) [12]. Irrespective of which microbe is used, several mechanisms like redoxolysis (redox reactions), acidolysis (formation of organic/inorganic acids), complexolysis (generation of complexing agents), and bioaccumulation [12, 35, 45] are involved in BL and the overall process' efficacy was determined by various factors like nutrient, oxygen availability, composition of leaching substrate, sensitivity of microbes to metals, pH, temperature, inoculum used, pre-culture period, BL period and state of solid residue [38, 46]. Only few BL systems were discussed in detail.

Aspergillus niger

Two methodologies were reported in the said process of BL using *A. niger*, i.e. one-step and two-step. In one-step process, the fungus was incubated with ash with no pre-culturing time while in two-step procedure pre-culturing of fungus was performed for different periods of time prior to incubation with fly ash [12, 40]. In general, two-step process resulted in better bioleaching as compared to one-step owing to higher spore germination and higher optimized pulp densities [12]. Further, easy handling and better control of optimization parameters in both the steps also make two-step approach a preferred choice [40]. But a comparison of parameters, i.e. pH variation, organic acids, and metals concentrations, metals extraction yield of these two processes showed the suitability of one-step bioleaching for treatment of low concentrations of fly ash (10–20 g L⁻¹) while for higher concentrations (40–50 g L⁻¹) two-step bioleaching was appropriate [47]. Pre-treatment like water washing (WW) can enhance the effectiveness of the BL process by removing all the water-soluble salts, i.e. alkali chlorides that are known to bond the heavy metals together, hence reducing the lag phase and BL period to a considerable extent [39, 40, 48]. In addition to that, optimization of various parameters like pH, fly ash pulp density (FAD), solid to liquid ratio (S/L), sucrose concentration, inoculum spore concentration, shaking speed and the time of addition of fly ash to the fungus when carried out at appropriate temperature (30 °C) and

Table 1 Comparison of different bioleaching systems used for removal of heavy metals from fly ash

Method	Approach	MO	FA type	Reaction conditions	Metals recovered	Metal removal (%)	References
BL	1-step & 2-step	<i>A. niger</i>	MSWI	FAD (1% w/v); 100 mL sucrose; 14 days, 30 °C, 120 rpm	Al, Mn, Zn; Cu, Pb; Fe	80–100; 60–70; 30	[12]
WW + BL	1-step	<i>A. niger</i>	MSWI	FAD (1% w/v); 100 mL sucrose; 30 °C, 140 rpm	Cd; Mn; Pb; Zn; Cr; Fe	99; 50; 28; 61; 18; 10	[39]
	2-step			Cd; Mn; Pb; Zn; Cr; Fe	96; 91; 73; 68; 35; 30		
WW + BL	1-step	<i>A. niger</i>	MSWI	FAD (5% w/v); 100 mL sucrose medium; 22 days, 30 °C, 110 rpm	Cd; Pb, Zn; Mn; Cu; Al; Fe; Cr, Ni	57; 52; 41; 33; 30; 12; <10	[40]
	2-step			FAD (5% w/v); 100 mL sucrose medium; 1 day, 30 °C, 110 rpm	Cd; Zn; Cu; Pb; Mn; Al; Cr, Fe, Ni	81; 66; 57; 52; 32; 27; <10	
BL	2-step	<i>A. niger</i>	MSWI	FAD (2.7% w/v); 150 g L ⁻¹ sucrose; 1.6 × 10 ⁷ mL ⁻¹ spore conc.; 8.5 days pre- culturing	Al	–	[46]
				FAD (2.7% w/v); 146 g L ⁻¹ sucrose; 0.3–2.3 × 10 ⁷ mL ⁻¹ spore conc.; 6.6 days pre- culturing	Fe	–	
				FAD (2.7% w/v); 153 g L ⁻¹ sucrose; 1.8 × 10 ⁷ mL ⁻¹ spore conc.; 9.3 days pre- culturing	Zn	–	
BL	1-step	<i>A. niger</i> metal resist- ant strain	MSWI	FAD (20 g L ⁻¹); 100 mL sucrose medium; 216 h, 30 °C, 140 rpm	Cd; Cr; Cu; Fe; Mn; Pb; Zn	87.6; 42.1; 69.7; 36.7; 98.7; 36.5; 68.5	[47]
	2-step			FAD (20 g L ⁻¹); 100 mL sucrose medium; 2 days pre-culturing; 216 h, 30 °C, 140 rpm	Cd; Cr; Cu; Fe; Mn; Pb; Zn	32; 25; 61; 25; 75; 2; 45	
WW + BL	2-step	<i>A. niger</i>	TPP	S/L (1 g 100 mL ⁻¹); 10 days pre-cul- turing; 6 h, 30 °C, 50 rpm	Cd, Co, Se, Ca, Cu, Mn, Fe, Al, Zn, Ti, V, B, K, Mg; Cr; Ni; As; Pb	100; 93; 83; 78; 70	[48]
BL	1-step	<i>A. niger</i>	MSWI	FAD (40 g L ⁻¹); 100 mL sucrose medium; 3 days, 30 °C, 140 rpm; pH 6.5	Al; Fe; Pb; Zn	78.7; 81.7; 76; 73.8	[49]

Table 1 (continued)

Method	Approach	MO	FA type	Reaction conditions	Metals recovered	Metal removal (%)	References
BL	2-step	<i>A. niger</i> metal resistant strain	MSWI	FAD (70 g L ⁻¹); 100 mL sucrose medium; 2 days pre-culturing; 288 h, 30 °C, 140 rpm; pH 6.6–7.8	Cd; Mn; Zn; Pb; Cr; Fe	87.3; 45.9; 49.4; 45.9; 21.5; 17.7	[50]
BL	2-step	<i>A. niger</i>	MSWI	FAD (1% w/v); 100 mL sucrose medium; 2 days pre-culturing; 30 °C, 120 rpm; pH 2.5–5.8	Fe; Al; Zn	56; 97; 98	[51]
BL	1-step	<i>A. niger</i>	CFA (lime calcified)	FAD (5% w/v); 35 °C, 250 rpm	Al	~60	[93]
BL		SOB	MSWI	FAD (1% w/v); 100 mL medium; 30 °C, 110 rpm	Cd, Cu, Zn; Al; Fe, Ni	>80; 60; 30	[44]
WW + BL		SOB + IOB	MSWI	S/L (50 g L ⁻¹); 6 days; 140 rpm	Zn; Al; Cd; Cu; Ni; Cr; Pb	81; 52; 100; 89; 64; 12; <1	[45]
BL		SOB	MSWI	FAD (1% w/v); 100 mL medium; 5 day pre-culturing; 28 °C, 120 rpm; pH 1.7	Cr; Cu; Zn; Cd; As	96; 73; 59; 100; 42	[53]
BL		IOB	MSWI	FAD (1% w/v); 100 mL medium; 5 day pre-culturing; 28 °C, 120 rpm; pH 1.7	Cr; Cu; Zn; Cd; As	100; 77; 100; 100; 49	[53]
BL		SOB + IOB	MSWI	FAD (1% w/v); 100 mL medium; 5 day pre-culturing; 28 °C, 120 rpm; pH 1.7	Cr; Cu; Zn; Cd; As	100; 67; 78; 100; 36	[53]
BL		SOB	CFA	FAD (10% w/v); 1 week pre-culturing; 28 °C, 200 rpm	Al; Fe	25; 15–22	[54]

BL bioleaching; WW water washing as pre-treatment, MO micro-organism, FA fly ash

rpm (100–140) can help in increasing the efficacy of the BL process [12, 39, 40, 44, 46, 48–52].

pH, an important growth parameter, was observed to decline slowly with the increase in FAD [12, 39, 40, 44, 49–52] owing to the formation of different acids (leaching agents) with varying concentrations. The concentration of these acids increases with increase in FAD in both approaches [12]. Wu et al. detected the formation of GA in addition to oxalic acid (OA) and CA in the presence of fly ash [12]. On the contrary, the studies conducted by Bosshard et al. showed GA to be the sole leaching agent generated in the presence of fly ash and CA in its absence [40]. The reason of contradiction in studies can

be attributed to the dependence of CA production solely on FAD while that of GA on other factors as well like sucrose concentration, spores concentration, time of addition [46] and the presence of Mn in fly ash [40]. Few studies claimed GA to be the main leaching agent in both the approaches [46, 47], while others designated it as a key factor only in one-step approach and CA in two-step approach [40, 48, 51].

Bioleaching of Al, Fe and Zn from MSWI fly ash followed pseudo-first-order kinetic model while that of Pb obeys second-order kinetic model [49]. A broad range of metals, i.e. Al, As, B, Cd, Co, Ca, Cu, Cr, Fe, K, Mn, Mg, V, Ti, Zn, Se, Ni, Pb, etc. (Table 1) were extracted using

Table 2 Comparison of metal leaching from fly ash using inorganic acids: chemical processes

FA type	Particle size (µm)	Leachate (conc.)	Reaction conditions	Metals recovered	Metal removal (%)	References
<i>H₂SO₄</i>						
MSWI	0.04–100	H ₂ SO ₄ (0.5 M)	S/L (1% w/v)	Al; Cu; Fe; Mn; Pb; Zn	80; 82; 30; 58; 10; 50	[12]
CFA	38–75	H ₂ SO ₄ (6.12 M)	S/L (100 g 400 mL ⁻¹); 6 h; reflux	Al ₂ O ₃	20	[61]
OFF	<500	H ₂ SO ₄ (0.5 M)	L/S (4 mL g ⁻¹); 25 °C; 24 h;	V; Al; Fe; Ni; Si	98; 68; 42; 12; 4	[62]
MSWI-SFA	0.25–4.97	H ₂ SO ₄ (5 wt%)	L/S (7 mL g ⁻¹); 5 min, 30 °C	Zn; Fe; Mg; Ca; Na; K; Al	90; 85; 75; 3; 40; 30; 3	[63]
OFF	–	H ₂ SO ₄ (0.5 M)	L/S (500 mL 100 g ⁻¹); 30 °C; 2 h; 400 rpm	V; Ni; Fe	65; 60; 42	[67]
MSWI	20–40	H ₂ SO ₄ (1.5 M)	L/S (10); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	60; 2; 81; 100; 82; 67; 58; 100; 98; 5; 100	[70]
MSWI	–	H ₂ SO ₄ (0.1 M)	L/S (40 mL g ⁻¹); 60 min; 25 °C; pH 3	Al; Ca; Fe; Cu; Zn; Pb	44.2; 100; 5.8; 52.4; 57.9; 28.3	[74]
MSWI-ESP	30	H ₂ SO ₄ (48%)	L/S (500 mL 20 g ⁻¹); 10 h; 25 °C	K; Na; Ca; Mg; Zn; Pb; Al; Fe; Cu; Sn; Cd; Mn; As; Cr; Ni; Hg	Total leaching 71.5%	[80]
CFA	0.5–10	H ₂ SO ₄	S/L (0.1% w/v); 48 h; 25–28 °C	Al, Fe	30	[81]
CFA	–	H ₂ SO ₄ (0.1 N)	10 g; lixiviant flow rate 230 mL/day/column; pH 1.2; 81 d	Hg	0.0013	[82]
TPF	10–90	H ₂ SO ₄ (0.5 M)	L/S (200 mL 100 g ⁻¹); 150–200 °C; 4 h	Al	84	[83]
CFA	74	H ₂ SO ₄ (50%)	180 °C; 4 h; high pressure	Al	82.4	[84]
CFA	–	H ₂ SO ₄	L/S (5:1); 200–210 °C; 80 min; 300 rpm	Al	87	[85]
PPF	75	H ₂ SO ₄ (19.47% v/v)	S/L (1.5 wt%); 80 °C; 2 h	V; Ni	94; 81	[87]
CFA (2 types)	–	H ₂ SO ₄ (0.1 M)	L/S (80–100 mL g ⁻¹); 24 °C; 20 h;	As	88–94	[86]
<i>HNO₃</i>						
MSWI	0.04–100	HNO ₃ (0.5 M)	S/L (1% w/v)	Al; Cu; Fe; Mn; Pb; Zn	90; 100; 30; 60; 60; 58	[12]
MFA (4-types)	0.3–1300	HNO ₃ (4 mol/L)	L/S (3–10 L kg ⁻¹); 5 min, 25 °C	Pb; Zn	7.8–10.6; 23.9–42.4	[68]
MSWI	20–40	HNO ₃ (3 M)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	67; 61; 48; 82; 58; 55; 36; 100; 66; 96; 72	[70]
MSWI	–	HNO ₃ (0.1 M)	L/S (40 mL g ⁻¹); 60 min; 25 °C; pH 3	Al; Ca; Fe; Cu; Zn; Pb	41.6; 100; 2.2; 52.8; 56.9; 25.3	[74]
MSWI-ESP	30	HNO ₃ (63%)	L/S (500 mL 20 g ⁻¹); 10 h; 25 °C	K; Na; Ca; Mg; Zn; Pb; Al; Fe; Cu; Sn; Cd; Mn; As; Cr; Ni; Hg	Total leaching 84.3%	[80]
CFA (2-types)	–	HNO ₃ (0.1 M)	L/S (80–100 mL g ⁻¹); 24 °C; 20 h	As	83–90	[86]
<i>HCl</i>						
MSWI	–	HCl (50 mmol/L)	S/L (10 g L ⁻¹); 30 °C	Cd; Cr; Cu; Fe; Mn; Pb; Zn	98; 3; 85; 1; 35; 20; 55	[47]

Table 2 (continued)

FA type	Particle size (μm)	Leachate (conc.)	Reaction conditions	Metals recovered	Metal removal (%)	References
MSWI-PFA	0.3–2.6	HCl (10 wt%)	L/S (7 mL g^{-1}); 5 min, 30 °C	Zn; Pb; Fe; Mg; Ca; Na; K	63; 40; 20; 58; 45; 10; 10	[63]
MSWI-SFA	0.25–4.97	HCl (10 wt%)	L/S (7 mL g^{-1}); 5 min, 30 °C	Zn; Pb; Fe; Mg; Ca; Na; K	94; 77; 100; 40; 15; 20; 5	[63]
MSWI	<125	HCl (1.0 M)	S/L (5 g L^{-1}); 3 h, 30 °C	Cd; Pb; Zn	–	[64]
MSWI	20–40	HCl (3 M)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	76; 63; 63; 86; 64; 58; 44; 100; 71; 100; 77	[70]
MSWI	–	HCl	L/S (30 mL g^{-1}); 15 min; 30 °C; pH 1	Pb; Zn; Fe; Cd; Cu; Al	86; 98; 82; 96; 62; 80	[73]
MSWI	–	HCl (0.1 M)	L/S (40 mL g^{-1}); 60 min; 25 °C; pH 3	Al; Ca; Fe; Cu; Zn; Pb	42.5; 100; 2.9; 50.2; 54.3; 14.8	[74]
MSWI-ESP	30	HCl (35%)	L/S (500 mL 20 g^{-1}); 10 h; 25 °C	K; Na; Ca; Mg; Zn; Pb; Al; Fe; Cu; Sn; Cd; Mn; As; Cr; Ni; Hg	Total leaching 85%	[80]
CFA (2-types)	–	HCl (0.1 M)	L/S (80–100 mL g^{-1}); 24 °C; 20 h	As	81–91	[86]
CFA	2.3	HCl (0.5 M)	S/L (1 g 100 mL $^{-1}$); 7 days; pH 7.4	Fe; Al; Mn; V; Cu; Ni; Zn; Cr; Ca; K	16010; 46700; 108; 174; 52; 34; 154; 40; 11400; 2290	[101]
Fly ashes from fossil fuel combustion (7 types)	1.5–22	HCl (0.5 M)	S/L (300 mg 30 mL $^{-1}$); 24 h	Al; Ca; Co; Cr; Cu; Fe; Mn; Ni; Pb; Si; V; Zn	11–95; 75–104; 26–69; 21–67; 37–104; 8–80; 46–110; 44–64; 34–89; 1–66; 51–165; 43–95	[88]
<i>HF</i>						
CFA (2-types)	–	HF (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	100	[86]
<i>Others</i>						
MSWI	20–40	Acidic Soln. from flue gas (0.2 M)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	<1; 19; <1; 92; <1; 53; <1; <1; <1; 1; <1; <1; 1; <1	[70]
CFA	–	H ₂ SO ₄ ; HNO ₃ (3:2)	L/S (1:20); 60 °C; 48 h	Al; As; Ba; Ca; Cr; Co; Cu; Fe; Pb; Mg; Mn; Ni; Se; Sr; V; Zn	165; 0.6; 46.5; 0.1; 1.35; 0.3; 0.7; 6.3; 0.5; 57.9; 11.4; 0.9; 1.5; 5.8; 0.3; 2.3	[88]

both one-step and two-step techniques, but one-step leaching resulted in higher removal of metals [47].

Sulphur and iron oxidizing bacteria

Chemolithotropic bacteria, i.e. *T. thiooxidans* (sulphur oxidizing bacteria, SOB) and *T. ferrooxidans* (iron oxidizing bacteria, IOB) [38] have also been used for fly ash BL either as pure or mixed cultures [45]. These bacteria convert insoluble metal sulphides to soluble metal sulphates [38]. H₂SO₄ is the main leaching agent in case of SOB [53, 54] and its attachment to sulphide or solid particles was mediated by

excretion of extracellular polymeric substances (EPS) [54]. In case of IOB, redox reactions are responsible for the mobilization of metals from solids. The electron transfer from metal to MO can occur by two processes, i.e. direct transfer involving physical contact between bacteria and fly ash or by biotic oxidation of Fe to III from II state resulting in solubilization of metals in solid [38, 45].

SOB is famous for its high tolerance to ash content, i.e. the media are able to resume pH and growth along with enhanced excretion of EPS with ash content as high as 10% [53, 54]. But studies had revealed that when high fly ash content (8%) was used only Zn (65%) and Cd (40%) were extracted significantly

Table 3 Comparison of metal leaching from fly ash using organic acids: chemical processes

FA type	Particle size (µm)	Leachate (conc.)	Reaction conditions	Metals recovered	Metal removal (%)	References
<i>CA</i>						
MSWI	0.04–100	CA (0.5 M)	S/L (1% w/v); 30 °C	Al; Cu; Fe; Mn; Pb; Zn	80; 100; 50; 30; 70	[12]
MSWI	–	CA (50 mmol/L)	S/L (10 g L ⁻¹); 30 °C	Cd; Cr; Cu; Fe; Mn; Pb; Zn	85; 30; 82; 25; 60; 60; 60	[47]
CFA (calcined)	<45	CA	PD (5%); 3 h;	Al	45	[93]
MSWI	–	CA (0.1 M)	L/S (40 mL g ⁻¹); 20 min; 25 °C; pH 3	Al; Ca; Fe; Cu; Zn; Pb	100; 93.1; 67; 100; 100; 96.6	[74]
CFA	<74	CA (0.3 M)	L/S (5 mL g ⁻¹); 30 °C; 24 h; 220 rpm	Cr	27.6	[92]
CFA	–	CA (1 mol/L)	L/S (1/50 mL g ⁻¹); 25 °C; 16 min; 30 rpm; pH 5	Sb	22–36	[94]
Smelter FA	–	CA (500 µM)	L/S (10 L kg ⁻¹); 25 °C; 14 h	Cd; Pb; Zn	–	[95]
<i>OA</i>						
MSWI	0.04–100	OA (0.5 M)	S/L (1% w/v); 30 °C	Al; Cu; Fe; Mn; Pb; Zn	85; 100; 60; 10; 68	[12]
MSWI	–	OA (50 mmol/L)	S/L (10 g L ⁻¹); 30 °C	Cd; Cr; Cu; Fe; Mn; Pb; Zn	10; 35; 79; 38; 72; 2; 57	[47]
CFA (calcined)	<45	OA	PD (5%); 3 h	Al	18	[93]
MSWI	20–40	OA (0.1 M)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	<4; 31; <1; 100; <1; 53; <1; 1; <1; 1; <1	[70]
MSWI	–	OA (0.1 M)	L/S (40 mL g ⁻¹); 20 min; 25 °C; pH 3	Al; Ca; Fe; Cu; Zn; Pb	43.3; 0.4; 46.5; 45.8; 44.9; 2.7	[74]
CFA	<74	OA (0.3 M)	L/S (5 mL g ⁻¹); 30 °C; 24 h; 220 rpm		8.6	[92]
Smelter FA	–	OA (500 µM)	L/S (10 L kg ⁻¹); 25 °C; 14 h	Cd; Pb; Zn	–	[95]
<i>AA</i>						
MSWI-PFA	0.25–4.97 µm	AA (20 wt%)	L/S (7 mL g ⁻¹); 60 min, 30 °C	Zn; Pb; Fe; Mg; Ca; Na; K; Al	62; 94; 8; 45; 47; 5; 5; 18	[63]
MSWI-SFA	0.3–2.6 µm	AA (20 wt%)	L/S (7 mL g ⁻¹); 60 min, 30 °C	Zn; Pb; Fe; Mg; Ca; Na; K; Al	97; 98; 45; 25; 20; 20; 3; 8	[63]
MSWI	20–40	AA (0.1 M)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	<4; 17; < 1; 70; < 1; 52; 2; < 1; < 1; < 1	[70]
MSWI	–	AA (0.1 M)	L/S (40 mL g ⁻¹); 20 min; 25 °C; pH 3	Al; Ca; Fe; Cu; Zn; Pb	88.4; 100; 23.2; 100; 100; 70.1	[74]
Smelter FA	–	AA (500 µM)	L/S (10 L kg ⁻¹); 25 °C; 14 h	Cd; Pb; Zn	–	[95]
<i>GA</i>						
MSWI	0.04–100	GA (0.5 M)	S/L (1% w/v); 30 °C	Al; Cu; Fe; Mn; Pb; Zn	95; 100; 80; 50; 72	[12]
MSWI	–	GA (50 mmol/L)	S/L (10 g L ⁻¹); 30 °C	Cd; Cr; Cu; Fe; Mn; Pb; Zn	80; 23; 78; 15; 30; 57; 50	[47]
MSWI	–	GA (100 mmol/L)	S/L (40 g L ⁻¹); 30 °C; 24 h; 140 rpm	Al; Fe; Zn; Pb	211.3; 81.4; 64.8; 40.91 ^a	[49]
CFA	<74	GA (0.3 M)	L/S (5 mL g ⁻¹); 30 °C; 24 h; 220 rpm		10.3	[92]
MSWI	–	GA (5%)	S/L (10 g 100 mL ⁻¹); 24 h	Cd; Cr; Cu; Ni; Pb; Zn	2.6; 1.6; 10.7; 0; 39.3; 54.7	[105]

Table 3 (continued)

FA type	Particle size (μm)	Leachate (conc.)	Reaction conditions	Metals recovered	Metal removal (%)	References
<i>Others</i>						
MSWI	20–40	FA (0.1 M)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	<4; 19; <1; 83; <1; 54; 3; <1; <1; 1; <1	[70]
MSWI	20–40	LA (1.0 M)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	<4; 37; <1; 100; <1; 66; 1; <1; <1; 43; <1	[70]
MSWI	–	LA (0.1 M)	L/S (40 mL g ⁻¹); 20 min; 25 °C; pH 3	Al; Ca; Fe; Cu; Zn; Pb	92.2; 100; 40.7; 100; 100; 62	[74]
MSWI	–	MA (0.1 M)	L/S (40 mL g ⁻¹); 20 min; 25 °C; pH 3	Al; Ca; Fe; Cu; Zn; Pb	99.7; 100; 80.2; 100; 100; 97	[74]
MSWI	–	TA (0.1 M)	L/S (40 mL g ⁻¹); 20 min; 25 °C; pH 3	Al; Ca; Fe; Cu; Zn; Pb	30.3; 6.7; 24.4; 32.7; 35.7; 4	[74]
<i>Mix</i>						
MSWI	–	CA + OA + GA (0.1 + 7.2 + 28.4 mmol/L)	S/L (10 g L ⁻¹); 30 °C	Cd; Cr; Cu; Fe; Mn; Pb; Zn	60; 25; 68; 18; 30; 20; 50	[47]
CFA (calcined)	<45	OA + CA (0.5 + 0.5 M)	PD (5%); 90 °C; 3 h;	Al	93.5	[93]
CFA	<74	CA + OA + GA (0.0317 + 0.0266 + 0.0625 M)	L/S (5 mL g ⁻¹); 30 °C; 24 h; 220 rpm	Cr	8.6	[92]

^a mg L⁻¹

while at low fly ash concentration (0.5–4%) most of the metals like Cd, Cu, Zn, Al and Ni are mobilized in appreciable amounts and only few (i.e. Cr and Pb) are solubilized in negligible amounts, i.e. 10 and 5%, respectively [44]. The initial addition of fly ash is known to halt the pH decrease and bacterial growth owing to its alkaline nature, presence of toxic metals and dilution effect [44, 54]. Therefore, pre-treatment of ash with HCl solution had shown enhanced growth rates [54]. Growth is further assisted by the use of co-cultures, sewage sludge as nutrient [44] and excretion of EPS that in turn is facilitated by the presence of Ba and Ca salts that provide solid surfaces to bacteria for attachment and growth [54]. Sulphur, being the main metabolic media, appreciably affects leachability of the system [44, 53]. BL of Pb by SOB is not a favourable process because of its conversion to PbSO₄ and hence immobilization [45].

In comparison to pure cultures, mixed cultures of SOB and IOB resulted in better extraction yield of the metals owing to the formation of both sulphate and ferric ions [45, 53]. Further in mixed cultures, consolidated effects of both the bacteria are able to overcome the disadvantages that independent strains have like poor tolerability of IOB to the high ash content and low metal leachability of SOB, hence imparting enhanced leachability and high tolerance to the system. Additionally, the buffering ability of mixed cultures impedes the drastic changes in pH as was the case in pure cultures. Also the decrease in concentrations of Fe³⁺ and SO₄²⁻ was observed with increasing ash concentration in pure cultures along with co-precipitation which was not observed in the case of mixed

cultures, thereby enhancing fly ash detoxification [53]. The release of Cu, in mixed cultures, was found to be dependent on IOB's metabolic activity and metals like Al, Cd, Cr, Ni, and Zn were extracted by the H₂SO₄ formed by SOB [45] while Cr was leached as a result of the combined effects of sulphate and iron [53]. The addition of FeSO₄, a substrate only for IOB, in mixed cultures impacts positively on the leaching of Cr, As and Cu but has no effect on Cd and Zn leaching. Moreover, addition of sulphur, a substrate for both SOB and IOB, increased Zn, Cd, As and Cr extractability when used at its optimum concentrations, i.e. 10, <5, 5 and 2 g L⁻¹, respectively. Factors like initial bacterial density and organic matter concentration have limiting impact on leaching of only a few metals; majority of metals extraction remain non-effected [53].

In addition to the famous combination of SOB and IOB, the inoculation of SOB with other *Thiobacillus* strains, i.e. *T. neapolitanus*, *T. acidophilus*, etc. had facilitated in attaining rapid and high percentage extraction of metals like Cd, Cu, Zn, Al, Fe and Ni [44].

Other microbial strains

Other strains like *Acidithiobacilli* sp., *Pseudomonas putida*, *Bacillus megaterium* were also used as bioleachates to extract metals from MSWI fly ash. All the three strains showed poor extractability of Cr metal (2–11%) while Ni was extracted in the range of 15–30%. For Pb, the extraction efficacy is very low except for *P. putida* which is around 30%. Independent studies have shown that *Acidithiobacilli*

Table 4 Comparison of metal leaching from fly ash using alkaline leachates: chemical processes

FA type	Particle size (µm)	Leachate (conc.)	Reaction conditions	Metals recovered	Metal removal (%)	References
<i>NaOH</i>						
OFF	<500	NaOH (2 M)	L/S (4 mL/g); 25 °C; 24 h;	V; Al; Fe; Ni; Si	90; 54; 0; 0; 8.5	[62]
MSWI-PFA	0.3–2.6	NaOH (3 M)	L/S (7 mL/g); 5 min, 30 °C	Zn; Pb	26; 84.3	[63]
MSWI-SFA	0.25–4.97	NaOH (3 M)	L/S (7 mL/g); 5 min, 30 °C	Zn; Pb	29; 45.7	[63]
OFF-EP OFF-CY	–	NaOH (2N)	L/S (500 mL/100 g); 30 °C; 2 h; 400 rpm	V; Ni, Fe	88; 0 78; 0	[67]
MFA (4-types)	0.3–1300	NaOH (3 mol/L)	L/S (5–30 L/kg); 30 min, 90 °C	Pb; Zn	15.0–18.7; 36.5–51.8	[68]
CFA (2-types)	–	NaOH (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	35–65	[86]
<i>Na₂CO₃</i>						
OFF	<500	Na ₂ CO ₃ (0.66 M)	L/S (4 mL/g); 25 °C; 24 h;	V; Al; Fe; Ni; Si	80; 0; 0; 0; 2.8	[62]
<i>NH₃ and its salts</i>						
OFF-EP OFF-CY	–	NH ₃ (4N)	L/S (500 mL/100 g); 30 °C; 2 h; 400 rpm	V; Ni, Fe	10; 59; 0 50; 55; 0	[67]
CFA	–	NH ₃ (1000 mg/L)	20–25 °C; 24 h; 130 rpm	Cu; Cd	0.5; 0.1	[97]
CFA	2.3	NH ₃ (10 mM)	S/L (1 g/100 mL); 7 days; pH 7.4	Fe; Al; Mn; V; Cu; Ni; Zn; Cr; Ca; K	13; 5240; 0; 44; 7; 5; 8; 7; 1510; 277	[101]
MSWI	20–40	NH ₄ Cl (0.1 M)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	<4; 21; <1; 89; <1; 54; 2; <1; <1; 27; <1	[70]
MSWI	20–40	NH ₄ NO ₃ (3.0 M)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	<4; 53; <1; 77; 16; 41; 4; 100; <1; 1; 29	[70]
<i>Mix</i>						
MFA (4-types)	0.3–1300	(NH ₄) ₂ SO ₄ + NaCl (1 + 5 mol/L)	L/S (5–30 L/kg); 60 min, 25 °C	Pb; Zn	14.0–17.3; 36.4–58.3	[68]

is able to extract >80% Cd, Cu and Zn, whereas high Cd leaching rates were noticed for *P. putida* [43]. A different type of bioleaching of MSWI fly ash was performed using thermophilic archaean *Acidianus brierleyi* grown on elemental sulphur which produces H₂SO₄ as a byproduct and able to leach 90% Zn within 9 days [33]. Another route based on utilization of 11 consortia derived from combination of 4 bacterial strains (*Micrococcus roseus*, *Bacillus endophyticus*, *Paenibacillus macerans* and *Bacillus pumilus*) for leaching of Fe, Cu, Ni and Zn from coal fly ash (CFA) showed that highest metal leaching occurred in consortia derived from the combination of last three MO [52].

Comparison of biological processes

Considering the alkaline nature of fly ash, fungal leaching seems to be a better option as compared to bacterial leaching owing to the ability of fungus to grow at high pH. Under similar conditions, bacterial growth is retarded, hence inhibiting their proper functioning. Further, the formation of organic acids that can undergo complexation with metal ions

had resulted in higher extractability of metals resulting in considerable reduction in fly ash’s toxicity. In spite of these advantages, the trade-off between process efficacy and cost in both the cases has to be considered. Subject to bacterial leaching i.e. SOB and IOB, the main energy sources are S and Fe which necessarily are not always present in required amounts in fly ash and hence have to be provided by external sources which increase the cost of process. But in case of fungal bioleaching systems, the operating cost is much higher than the bacterial leaching system, because the need of proper bioreactors, good aeration, carbon source, organic acid excretion, etc. makes it a less preferred choice [12, 41, 55, 56].

Physical process

Carrier-in-Pulp method (CIP) is employed for recovering heavy metals from Molten Fly Ash (MFA) while using adsorbent made up of activated carbon or other materials, e.g. Fe in a powder form [57, 58]. NaCl was employed as a leaching agent to facilitate the process followed by physical

separation techniques to recover the carrier from the leachate. Good to moderate recoveries in range of 50–90% were achieved by use activated carbon as sequenchor for metals Zn, Pb, Cu and Cd [57] while very high leaching rate i.e. 97–99% was attained for Pb, Zn, Cd, and Cu when Fe powder was used [58]. The CIP methodology is very effective in inhibiting the heavy metals' solubility far below the disposal guidelines and hence ensuring safe landfill dumping [57]. Similarly, a melting approach was designed to extract Zn from fly ash by partitioning it into the gas phase [59].

Chemical process

Hydrometallurgical process owing to its simplicity and cost-effectiveness is also used for detoxification of fly ash [57]. Targeted metal extraction is usually conducted using this method for metals like Ga [60], Al [61], V [62], Pb, Zn [63], etc. Simple to complicated approaches were used involving special reactors, fusion, extractions, precipitation or crystallization independently or in combination with each other or other methods [60–66]. Various factors like acid or alkali molar concentration, pH, liquid/solid (L/S) ratio, leaching time and temperature, particle size, presence of impurities, retention time, type of leaching agent, type of fly ash have considerable effect on the leaching efficacy of hydrometallurgical process [60–63, 66].

Lixivants like acids [63, 64], base [62, 67] or a combination of acid–base [63, 66] or acid–salt [64] for removal of metals were researched and it was observed that the type and concentration of leaching agents used affected the leaching efficiency to considerable levels and can alter the selectivity of metal leaching and the speciation of the metals [62–64, 66]. The type of fly ash had also shown to impact the efficacy of the leaching process and lixivants' selection [68]. Moreover, the phases in which metals are present at various experimental pH also impact the extractability as also simulated by the MINTEQA2 [69]. Overall the leaching using different lixivants had resulted in increase in particle size of fly ash except deionized water [70].

Leaching with water

Leaching using either acids or bases is usually a two-step process, initiated by preliminary WW followed by acid or base washing. Simple WW can be used to remove the surface metals leading to exposing the nucleation elements which can then be removed by further WW leaving insoluble metals behind [65] and, hence, accompanied by a reduction in particle size [70, 71]. This not only avoids the extra protocols that may be required to leach metals by other methods, but it also saves the considerable amount of acid/base that otherwise may be required to leach simple metals like Na, K, Mg and Ca [63, 72–75] that can be water extracted from

fly ash in just 5 min [73, 74]. Some other metals also gets washed away with water like Zn, Cd, Pb, Al [20, 64, 73–76], Mo, Se [77], Mn, Co, Fe [20, 75], As, Sr [78], etc. The leaching rate of water soluble metals is $B > Mo > Se > Li > Sr > Cr > As \sim Ba \sim Cd \sim V > Sn > Rb \sim Zn > Cu \sim Ni \sim Pb > U > Co > Mn$. Heating has a positive impact on the leaching of metals like Al, Si, K, Na, Ba, Cr, Rb, Sr, and V, while Ca and Fe leaching remained constant [71]. Leaching of metals, especially Ca from fly ash, can further be enhanced using a series of extraction steps using deionized water and heating [74, 75]. On the other hand, treatment of medical waste incinerator fly ash (MWIFA) with supercritical water (SW) and combination of SW + H₂O₂ resulted in stabilization of heavy metals except Cd and As that showed enhanced leaching after treatment [79].

Leaching from inorganic acids

Simple stirring of fly ash with varying molar concentrations of acids followed by washing of residue was used to access the leaching potential of the acids used. The detailed view of reaction conditions and acids used in this regard is given in Table 2. Acid leachability depends on the type of fly ash and acid used [68]; overall the order of total metal solubility for treatment of fly ash with different acid combinations is as follows: aqua regia > HCl > HNO₃ > H₂SO₄ [80]. H₂SO₄ is not considered the best choice because of its poor ability as a dissolving agent as well as the formation of insoluble sulphates that can coat on the surface of fly ash making it insoluble [81].

Poor extractability of Pb is shown in H₂SO₄ [12, 68, 73, 74] as well as in dilute HNO₃ and HCl [74], while good leaching was observed in concentrated solutions of HNO₃ [12, 80] and HCl [63, 64, 73, 80]. The formation of PbCl₄²⁻ is known to favour the leaching process in later cases as against the formation of PbCl₂ insoluble salt [73]. Almost negligible leachability of Hg was also observed in dilute and concentrated H₂SO₄ [80, 82]. Experiments conducted for other metals using 0.5 M H₂SO₄ and HNO₃ showed that metals extractability is almost same in both the acids for MSWI fly ash with order: Cu (100%) > Al (80–90%) > Mn (60–65%) > Zn (50–60%) > Fe (30%) [12]. Same molar solution of H₂SO₄ also facilitated the leaching of valuable metals like V, Ni, Ti and Al from oil-fried fly ash (OFF) and thermal power station fly ash (TPF) [62, 67, 83]. Efficacy of Al extraction in H₂SO₄ can be enhanced by carrying out the reaction in high-pressure vessel [84] or high temperature [62, 85] which facilitates phase change and hence increasing solubility [84]. In case of Fe, almost negligible leaching (2–6%) is reported in 0.1 M H₂SO₄, HCl and HNO₃ [74] which enhance considerably (82–100%) at very low pH by use of concentrated acid solutions [63, 70, 73]. Similar behaviour was also observed for Mn and Si

[70]. Complete removal of As has been achieved from two different types of CFA using 0.1 M HF (100%), while equimolar concentrations of other acids like H₂SO₄, HNO₃ and HCl had been able to leach 80–94% As which is present in the form of either As₂O₅ or Ca(AsO₄)₂ [86]. Simple 19% v/v H₂SO₄ extraction of power plant fly ash (PPF) leads to simultaneous recovery of 94% V and 81% Ni at 80 °C [87]. Combination of H₂SO₄ and HNO₃ (3:2) was used to leach a range of metals including Al, As, Ba, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Se, Sr, V and Zn in significant amounts [88].

Different factors affect the efficacy of process depending on the type of metal in concern. Extraction of Zn and Cd is highly dependent on the concentration of acid rather than the type of acid used [63, 64]. Leaching of Pb decreases with increase in extraction time while that of Cd and Cr remains same in all the three acids except that Cr showed that 45% decreases leaching in HNO₃ [89]. Further, extraction efficacy was found to be temperature independent of Pb and temperature dependent for Zn [63], Al [83, 85], Ni and V [87]. Using low L/S ratio facilitates fast (15 min) and 100% leachability of Cd and Zn and 80–90% extraction of Fe, Pb and Al owing to the formation of Ca₂PbO₄, CaSi₂O₅, Pb₅SiO₇, Ca₃Al₂Si₃O₁₂ and SiO₂ in leachate [73]. In case of Al, acid leaching process efficiency is dependent on the formation of glassy phase and is inhibited with increase in S/L ratio and acid concentration owing to mass transfer and self-inhibition effects imparted by the presence of Ca in the fly ash; on the other hand, stirring time and temperature have a positive effect on leaching efficiency [90]. Particle size of fly ash also impacts the leachability of metals to a minor extent [76].

Studies had also shown that acid extraction if facilitated by microwave can result in better leachability of the metals and in shorter time span [91]. High extractability, i.e. >90% of metals like Pb and Zn and >80% of Ni and Cd can be carried out in just 7 min [91].

Leaching from organic acids

Organic acids like oxalic acid (OA), citric acid (CA), gluconic acid (GA), lactic acid (LA), acetic acid (AA), oxalic acid (OA), tartaric acid (TA), formic acid (FA) and malic acid (MA) either independently or in combination are used to leach metals like Cd, Al, Cu, Fe, etc. [12, 47, 70, 74, 92]. In case of coal fly ash, Cr forms the most stable complex with CA resulting in the highest leaching among the set of three, i.e. CA, GA and OA; the order of percentage leaching was CA > GA > mixed acids > OA [92] while Al showed an increase in leachability, i.e. ~93% in combined 0.5 M OA-CA (1:1) solution as compared to when independent acids were used [93]. Similar order of leaching as for Cr in the previous case was observed for other metals in case of MSWI fly ash [47] but for Cu leaching was same in all the three acids with almost 100% leaching, irrespective of their

concentration used [12]. In case of Al, Fe, Mn, Pb and Zn, the amounts of metal leached depends on the concentration of acids employed; the order of leaching observed with 0.5 M acid concentration is: GA > OA > CA for Al (80–100%) and Mn (60–80%); OA > GA > CA for Fe (20–50%); GA > CA > OA for Pb (10–50%) and OA ~ GA ~ CA for Zn (50–70%) [12]. On the contrary, the leaching of Mn, Cd, Cr and Cu was almost negligible from high metal content fly ash when 100 mmol L⁻¹ GA was used for extraction which might be attributed to the very high levels of toxic metals present in the ash [49]. The leaching of Al, Ca, Fe, Cu, Zn, Pb was nearly same in LA and AA; OA and TA; MA and CA the highest being observed for Ca. Considering the fact that oxalates and tartrates of respective metals are sparingly soluble in water, minimum leaching was recorded with OA and TA while nearly 100% leaching of all the metals except Fe (80 and 67%) was achieved in MA and CA [74]. Low concentrations of AA, FA, OA and LA are able to leach Na and K effectively, while Fe, Mn and Si are poorly soluble [70]. A strong relationship was observed between the concentration of acid, pH, time of extraction and extraction yield for MSWI fly ash. The yield increased from 40 to 90 in case of Zn and 50–90 for Pb when AA concentration changes from 5 to 20 wt% [63]. Good extractability of Cd and Pb in AA was achieved within 10 min but the extraction percentage of Pb decreased with increase in extraction time [89].

Hg is highly extractable in AA as opposed to H₂SO₄ and Na₂CO₃ [82] while only 22–36% Sb is leached in CA; the rest being bound in coal fly ash [94]. Another study on smelter fly ash claimed extraction of metals like Pb, Cd and Zn in organic acids (CA, AA, OA) to be more dependent on pH rather than the type of acid used [95].

An interesting phenomenon regarding organic acids was discovered by Huang et al., who found out that these acids act in pairs with respect to leaching behaviour towards metals; the order of extraction is CA ~ MA > AA ~ LA > OA ~ TA [74].

Leaching with alkaline leachates

Considering the cost-effectiveness, alkaline leaching is considered a better choice as compared to acid leaching [68]. As in case of acid leaching, concentration of alkaline leachates also has a considerable effect on the extraction process [67]. Among NaOH, NH₃ and Na₂CO₃ solutions (Table 4), NaOH was found better lixiviant for V (80–90%) [62, 67] as well as for Al (54%) [62] while the rest of the two (NH₃ and Na₂CO₃) showed better extractability just for Ni (60%) [67] and V (80%) [62], respectively. On other hand, none of these led to promising Fe extraction owing to its occurrence as base insoluble FeSO₄·7H₂O [67]. Arsenic also showed poor extractability in alkaline solutions [86].

Low solubility of Zn (~30%) and enhanced Pb extractions (80%) were achieved in high normality NaOH (3N) but this was accompanied by the formation of gelatinous precipitates that hinder the filtration process [63]. The process showed dependency on temperature for Pb and independency for Zn [63]. 100% extraction of Cu was achieved in NH_4NO_3 while NH_4Cl is able to leach 89% K [70].

The leaching behaviour of different metals with alkaline leachates is defined by the nature of metals and their forms available in the fly ash [63, 66]. Leachates hydroxides react with divalent metals to form simple $\text{M}(\text{OH})_2$ [66], while the metals having the amphoteric nature like Pd, Zn and vanadium oxides result in the formation of complex ion species like $\text{Pb}(\text{OH})_3^-$, $\text{Zn}(\text{OH})_3^-$, HV_2O_5^- , H_2VO_4^- , $\text{VO}_3\text{OH}^{2-}$ and $\text{V}_2\text{O}_7^{4-}$ which are responsible for high extraction rates [66, 67, 96]. In case of Pb, poor extractability was observed in alkaline media if forms other than oxide are present [63]. NH_3 is also known to favour extraction of Cu and Cd in addition to Ni owing to the formation of metal-ammonium complexes like $(\text{Ni}(\text{NH}_3)_x)^{2-}$, $(\text{Cu}(\text{NH}_3)_x)^{2+}$ [67, 97].

Leaching with chelating agents

Selection of chelating agents (Table 5) plays a very important role in controlling efficacy and cost of the leaching process [30]; also the leaching in this case is independent of pH [98]. Ethylenediaminetetraacetic acid (EDTA) is used in the majority of cases to leach the metals [70, 86, 98–100] and found to have good lixiviant for most of the metals like Mg, Ca, Al [99], Se, Mo [77] and V in high yields but is not a good extractant for potassium containing aluminosilicates core metals [101] and Fe, Al and Si [70] with process highly dependent on pHs.

Good extractability of EDTA and diethylenetriaminepentaacetate (DTPA) in contrast to Nitrilotriacetic acid (NTA) was observed for Cr (20–50%), Cu (60–95%), Pb (60–100%) and Zn (50–100%) in a pH range of 3–9 [98]. Leaching of As from CFA was carried out using various chelating agents [ammonium acetate (NH_4OAc), sodium gluconate (SG), EDTA, iminodiacetic acid (IA), trisodium citrate dehydrate (TSC), potassium dihydrogen citrate (PDC), disodium hydrogen phosphate (DSHP), potassium dihydrogen phosphate (PDP), glucose and sucrose] and shown to depend strongly on the rate of dissolution of Fe and Al. Reasonable leachability of As hence was observed only in case of TSC (68%), EDTA (70%), IA (78%) and PDC (83%) while glucose and sucrose showed very poor extractability (4%) [86]. The presence of Fe and Al in the fly ash is known to favour the complex formation of As by the formation of some intermediate complexes [86]. Ge (98.8%) from CFA can be isolated first by leaching with catechol (CAT) followed by precipitation with CAT and cetyl trimethyl ammonium bromide (CTAB), but the process is hindered

by the presence of other metals [102]. Three types of IA containing chelating resins, i.e. Lewatit TP-207, Purolite S-930 and Amberlite IRC-748 were used in the presence of sulphate solution for leaching of Ni from Orimulsion fly ash (OFA) which is rich in Ni and V; after preliminary leaching of V and Fe, the best results were obtained for TP-207 [103]. Another set of chelating leaching agents employed obeyed the leaching order of: EDTA ~ citric acid > histidine > glycine for a range of metals. Cysteine on the other hand resulted in formation of cystine precipitates and hence proved to be quite ineffective for leaching of metals [101].

Though the high percentage of metal extraction was achieved by chelating agents, but their use for detoxification of fly ash is hampered because of high cost and also due to difficulty in heavy metals' recovery from the chelated complex. For that purpose, certain green methods were also adopted for the extraction of heavy metals from fly ash. Saponin, a plant-derived chemical, is used by several researchers for the heavy metals' leaching [99, 104] and is found to be equally effective as that of EDTA [99]. The method efficacy depends to larger extent on pH, S/L ratio and ionic strength while minor contributors are saponin concentration, temperature and extraction time [104]. The method is able to extract 20–45% Cr; 50–60% Cu; 100% Pb; 40–50% Zn; 50–100% Mg; 60–70% Ca and 10% Al. Sequential extraction using three different triterpene-glycoside types of saponins was also used for extraction of Cr, Cu, Pb and Zn [99]. Another environmental friendly approach employed for heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) leaching from fly ash makes use of molasses hydrolyste which acts as a strong chelating agent. This hydrolyste is able to extract large amount of metals as it is workable at pH at which incinerator fly ash are collected [105]. Use of canine serum is also helped in the extraction of Co, Ni, Cu and Zn from 7 different types of ashes with leaching efficiency of 40–90% [106] and is also able to leach other metals like Al, Fe, Ca, K, V, Mn, Ni and Cr in percentages much better than simulated serum solution [101]. On the contrary, poor extractability of Ca, Mg, Al, Fe, Ti, etc. was observed in humic acid [100].

Leaching using a combination of different leachates

To enhance the efficacy of extraction process, researchers tried various combinations of leachates. Fusion of CFA with NaOH at temperatures ranging between 300 and 800 °C followed by WW resulted in only 35% Al extraction [107]. 100% leaching of Al along with the recovery of Si in forms of sodium silicate and amorphous SiO_2 was achieved using a two-step approach: employing simple treatment of CFA with hot H_2SO_4 in a first step and a combination of Na_2CO_3 , H_2O and H_2SO_4 in a second step [108].

Reasonable absorption of Pb, Cd and Zn, i.e. 85, 83, and 65% was accomplished with use of binary mixture of 1 M

Table 5 Comparison of metal leaching from fly ash using chelating agents: chemical processes

FA type	Particle size (µm)	Leachate (conc.)	Reaction conditions	Metals recovered	Metal removal (%)	References
MSWI	20–40	EDTA (0.1 M) (pH adjusted)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	<4; 65; <1; 97; 40; 40; 5; 100; 25; 94; 40	[70]
MSWI	20–40	EDTA (0.1 M) (pH not adjusted)	L/S (5); 24 h	Al; Ca; Fe; K; Mg; Na; Si; Cu; Mn; Pb; Zn	<4; 19; < 1; 82; < 1; 35; 2; < 1; < 1; 34; 1	[70]
Fly ash (2-types)	–	EDTA (0.1 mol/L)	S/L (5 g/50 mL)	Ca; Al; Fe; As; K; Mg; Ba; Ti; Mn; Cu	1000; 1800; 1500; 100; 100; 120; 20; 120; 6; 0	[100]
CFA (2 types)	–	EDTA (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	70	[86]
MSWI (5 types)	–	EDTA (3%)	20 °C; 24 h;	Cr; Cu; Pb; Zn	20–50; 60–90; 60–100; 50–100	[98]
MSWI (2 types)	–	EDTA (3%)	–	Cr; Cu; Pb; Zn	20–35; 60–70; 80–90; 60–90	[99]
CFA	2.3	EDTA (10 mM)	S/L (1 g/100 mL); 7 days; pH 7.4	Fe; Al; Mn; V; Cu; Ni; Zn; Cr; Ca; K	2030; 4050; 23; 108; 15; 6; 20; 28; 1630; 175	[101]
CFA (2 types)	–	Glucose (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	4	[86]
CFA (2 types)	–	Sucrose (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	4	[86]
CFA (2 types)	–	Na ₂ HPO ₄ (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	5–9	[86]
CFA (2 types)	–	NH ₄ OAc (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	6–8	[86]
CFA (2 types)	–	PDP (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	36	[86]
CFA (2 types)	–	SG (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	61–71	[86]
CFA (2 types)	–	TSC (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	55–68	[86]
CFA (2 types)	–	PDC (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	83	[86]
CFA (2 types)	–	IA (0.1 M)	L/S (80–100 mL/g); 24 °C; 20 h;	As	78	[86]
OFA	–	IA–Lewatit TP-207	–	Ni	–	[103]
MSWI (5 types)	–	DTPA (3%)	20 °C; 24 h;	Cr; Cu; Pb; Zn	20–50; 60–90; 60–100; 50–100	[98]
MSWI (5 types)	–	NTA (3%)s	20 °C; 24 h; pH 3–9	Cr; Cu; Pb; Zn	20–50; 60–90; 5–10; 20–50	[98]
CFA	–	CAT–CTAB	CAT/Ge (8.4); CTAB/Ge (5.1)	Ge	95	[102]
OFA	–	Purolite S-930	–	Ni	–	[103]
OFA	–	Amberlite IRC-748	–	Ni	–	[103]
CFA	2.3	Histidine (10 mM)	S/L (1 g/100 mL); 7 days; pH 7.4	Fe; Al; Mn; V; Cu; Ni; Zn; Cr; Ca; K	340; 0; 15; 31; 7; 4; 18; 5; 230; 69	[101]
CFA	2.3	Glycine (10 mM)	S/L (1 g/100 mL); 7 days; pH 7.4	Fe; Al; Mn; V; Cu; Ni; Zn; Cr; Ca; K	35; 0; 12; 16; 6; 4; 4; 1; 3180; 114	[101]
CFA	2.3	Na-Citrate (10 mM)	S/L (1 g/100 mL); 7 days; pH 7.4	Fe; Al; Mn; V; Cu; Ni; Zn; Cr; Ca; K	1860; 3100; 22; 114; 12; 7; 19; 22; 5280; 87	[101]
MSWI (2 types)	–	Saponins (3%) 4 types	S/L (0.5 g/25 mL); 20 °C; 24 h; pH 4	Cr; Cu; Pb; Zn	20–45; 50–60; 80–100; 50–80	[99]

Table 5 (continued)

FA type	Particle size (μm)	Leachate (conc.)	Reaction conditions	Metals recovered	Metal removal (%)	References
Fly ash (2-types)	20; 30	Humic acid	S/L (5 g/50 mL)	Ca; Al; Fe; As; K; Mg; Ba; Ti; Mn; Cu	300; 0; 200; 50; 0; 40; 10; 15; 5; 7	[100]
MSWI		Molasses hydro- lysate (1.8%)	S/L (10 g/100 mL); 24 h	Cd; Cr; Cu; Ni; Pb; Zn	2.5; 3.1; 23.1; 0.3; 60.1; 353.3	[105]
CFA	2.3	Synthetic serum (10 mM)	S/L (1 g/100 mL); 7 days; pH 7.4	Fe; Al; Mn; V; Cu; Ni; Zn; Cr; Ca; K	82; 370; 14; 31; 9; 12; 8; 6; 2960; 77	[101]
CFA	2.3	Dog serum (10 mM)	S/L (1 g/100 mL); 72 h; pH 7.4	Fe; Al; Mn; V; Cu; Ni; Zn; Cr	515; 1124; 10; 61; 43; 6; 236; 12	[101]
MSWI	–	Serum (41.2 g/L)	S/L (1%); 13.54 h; 23.4 °C	Cu; Zn; Pb; Cd	55.1; 6.2; 17.8; 78.1	[104]
Fly ashes from fossil fuel combustion (7 types)	1.5–22	Canine serum	S/L (300 mg/30 mL); 24 h	Al; Ca; Co; Cr; Cu; Fe; Mn; Ni; Pb; Si; V; Zn	83.5–7000; 7.8–42.3; 855–3.6; 2.6–197; 312– 13200; 8.7–225; 10.2–24500; 0.2– 274; 21.5–1850; 132–1860	[106]

HCl + 1 M NaCl solution [64]. Equally good results were observed for the three metals when serial batch test employing HNO₃ and slaked lime was carried out but the process is highly pH dependent [66]. Comparatively higher extractions of Pb (97%) as well as Fe (100%) and nearly same leaching of Zn (68%) were achieved using simple acid–base coupled extraction, i.e. NaOH leaching followed by HCl leaching [63]. The process is observed to be dependent on pH, L/S ratio and concentration of acids and alkali used [63, 66]. Positive correlation was observed in the percentage extraction of Zn, Fe and Pb with an increase in HCl concentration [63, 64]. A three-step process was adopted for recovery of high purity Ga and V from CFA by treating the H₂SO₄ leachate first with imminodiacetic acid containing chelating resin and then with either di(2-ethylhexyl)phosphoric acid (D2EHPA) or tri-*n*-octylmethylammonium chloride (TOMAC) [109].

A range of metals (Cd, Cr, Cu, Mo, Pb, Zn, As, Co, V, Ni, Ba) was also extracted using 2^{4–1} fractional factorial design consisting of 5 step sequential extractions using (1) HNO₃ acidified distilled water, (2) AA, (3) NH₂OH-HCl, (4) H₂O₂ + CH₃COONH₄ and (5) HF + HNO₃ + HCl. These were able to extract metal chlorides and sulphates; metal carbonates; oxides of Mn and Fe; metal sulphides and crystallized oxides, respectively [110]. Similar sequential extraction when performed for the removal of heavy metals, i.e. Cd, Co, Cu, Ni, Pb, Sb, and Zn resulted in 1.5–36.4% of the total element content from six different types of coal-fired power plant fly ashes [111]. Cr and Cu are also extracted using same approach [112]. The same setup when used microwave heating resulted in much higher removal efficacies of the metals like Zn, Pb, Cu, and Cr within 2–6 min while for Cd the leaching efficiency was

comparable to that of traditional HCl extraction method [113]. Recirculation loop experiment, consisting of 10 loops, was designed based on closed circuit of alkaline washing, acid washing and precipitation, is able to remove 21% Cd, 99% Pb, 100% Al and 63% Zn [114]. Use of 7-step sequential extraction employing water, MgCl₂, NaOAc, NH₂OH·sHCl, NH₄OCOCOONH₄·H₂O, NaOCl and microwave digestion with HNO₃ resulted in the removal of As, Cr, Cu, Fe, Pb and Zn from CFA [115].

Electrochemical processes

Electrolysis processes like electrochemical remediation (EDR), cyclic voltammetry (CV), etc. have been studied by various researchers as alternate to already existing techniques for removal and recovery of metals from fly ash. The technique is good for those fly ashes which are chloride-rich making majority of metals to be available in the water-soluble chloride form [116].

EDR detoxifies the fly ash by separation of metals from fly ash by dissolution, acidification and membrane separation [32]. Factors like current density, remediation time, L/S ratio, and assisting agent were assessed as contributors towards the efficacy of the process [32, 117–119]. A 3-compartment cell with applied current of 50 mA was found effective in removing Cd (60%) and Zn (45%) from MSWI fly ash while for rest of metals (Al, As, Ba, Cr, Cu, Mn, Ni, Pb) <20% removal was achieved [32]. An even lower applied current 40 mA when employed in 5-compartment cell at pH 2 led to very high removal of Cd (85–120%) from power plant fly ash [118], whereas 5.6 mA cm^{–2} constant current supply and use of 4-compartment cell resulted in 97% Cd removal from Electrostatic precipitator fly ash (ESP

ash) after 36 days [120]. The change in current density does not show the strong impact on percentage of Cd extracted when the sequential extraction process is used [119]. To assist the EDR process, the role of assisting agents was also researched and it was suggested that best results can be obtained for the ones that form stable complexes but the type of metal and nature of fly ash do play their role [117]. Use of ammonium citrate as assisting agent helped in increased removal of Cu (~70%) and almost same Cd (>70%) recovery within 3 weeks that increased to >80% for both metals in 70 days along with appreciable separation of other metals (Pb, Zn, and Cr) [121]. But studies have shown that the best choice for combined removal of metals is solution of 0.25 M ammonium citrate and 1.25% NH_3 [117]. Almost 100% Cd removal was achieved when 2.5% NH_3 was chosen as assisting agent. On the other hand, the addition of sodium and ammonium citrates favours Cu and Pb removal, respectively [117]. Use of CA in place of sodium citrate facilitates removal of Ni and Cu and use of 2.5% NH_3 favours higher Cd extractions due to the formation of tetraamine complexes [117].

EDR was also used to treat fly ashes from straw (SF) and able to remove 78% Ni, 66% Pb and enhanced level (97%) of Cd when scale-up process is used. On the other hand, EDR of co-combustion of wood (CWF), a high metal content ash, did not give encouraging results [122]. The use of assisting agent though facilitates the fast and effective removal of heavy metals, but on the other hand can impede fly ash further valorization due to strong binding capacity with fly ash causing impregnation of assisting agent in fly ash [122].

A similar set of experiments conducted with and without assisting agent, Na-gluconate, as a metal solubilization enhancer showed comparatively higher metal extraction rates in EDR [116].

Thermal treatment processes

High temperature treatment of fly ash was also done to aid detoxification of fly ash. Volatilization of metals is determined by many factors like time, temperature, metal species involved, type of matrix, etc. [123] and is governed by simple first-order rate law [124]. Use of assisting agents promotes the evaporation of metals at a comparatively low temperature. Roasting of fly ash with chlorine is one such way that can be done by direct chlorine gas, HCl fumes or by the use of some salt like NaCl, CaCl_2 , etc. [124–129]. The process can also occur by thermal treatment of chloride rich fly ash, hence promoting the vaporization of metals [123, 130]. Temperatures, gas velocities, chloride concentrations, residence times [127] and type of assisting agent used [125] impact the removal rate of metals to considerable level. In addition to these the presence of alkali metals and moisture

owing their high affinity towards chlorine effects process efficiency [123].

Among the three chlorinating agents, i.e. CaCl_2 , MgCl_2 and NaCl, the first two are known to better agents than NaCl owing to its low volatilization temperature evaporates without reacting [125]; the best being CaCl_2 [125, 128]. Hence, by using MgCl_2 90% extractability was achieved for metals Cu, Pb and Zn [125], whereas CaCl_2 leads to the removal of >90% Cd and Pb [125, 127, 128]; 100% Cu [125, 128], and 90% Zn [125, 127, 128] and 75% Ni [125] from MSWI fly ash. On the other hand, treatment of fly ash with CaCl_2 promoted just 13% Cr extraction from simulated sample [126] while in actual fly ash case CaCl_2 imparts negative impact on Cr leaching from fly ash [125]. Polyvinyl chloride (PVC) doping of power plant incinerator fly ash was also done as a source for chlorine and it was observed that it leads to 10–15% increase in heavy metals' (Pb, Zn and Cd) vaporization at temperatures <1000 °C [131]. Extractability of Cr from MSWI fly ash spiked with 5% Cr_2O_3 followed by sintering was found dependent on the temperature and atmosphere provided as it affected the formation of soluble oxides [132].

The composition of fly ash also impacts the efficacy of chlorination-assisted thermal treatment process; it is observed that the presence of SiO_2 favours the reaction of metals with CaCl_2 , thereby facilitating detoxification of sewage sludge ash (SSA) in just 10 min, while the presence of CaO and Al_2O_3 in MSWI fly ash hinders the reaction resulting in delayed metals' evaporation [128]. Leaching of Ca and Mg from CFA calcinated at similar temperature followed by NH_4Cl solution washing at 80 °C had shown to depend on the phases in which the respective metals are present in fly ash [72]. Extraction efficiencies of 81, 70 and 60% for Al, Fe and Ti were obtained by thermal treatment of CFA at 1200 °C with CaO followed by H_2SO_4 leaching at 80 °C. The process is recommended for high percentage removal of Al that occurs in acid insoluble form, i.e. mullite [61]. Likewise, CaO presence in the fly ash helps in extraction of Cr that at high temperatures reacts with Cr to facilitate its extraction in acetic acid [133].

Another approach is based on the calcination of MSWI fly ash with H_2SO_4 at 300 °C resulting in cracking of fly ash core and formation of aluminium sulphate followed by recovery of unreacted H_2SO_4 ; the process resulted in 85% alumina extraction with the added advantage of avoiding excess use of acid [134].

The high impact of evaporation temperature, sintering atmosphere, velocity of gas stream and the presence of some cations or anions on the thermal recovery of metals and evaporation time was observed [31, 124, 129, 135]. Metals like Cd and Pb are almost completely extracted at temperatures ranging between 760 and 1300 °C, while complete Cu extraction was observed at 1030 °C in air as against 10%

in argon atmosphere. On the other hand, Zn showed better extractability in argon atmosphere (100%) as compared to air (51%) at 1130 °C [31]. Cr extraction is favoured in the air owing to the formation of hexavalent oxides as compared to in N₂ atmosphere [132]. The extraction efficacy of Cu and Zn, the least volatile metals [31], and Pb decreases with increasing temperature whereas that of Cr increases [132]. Comparatively low temperature evaporation can be facilitated in much shorter time by use of chlorinating agent, e.g. NaCl [124], CaCl₂, Cl₂ [129, 136]. Further, the velocity of gas stream when changes from low to high can enhance metal evaporation rate and in much less time too [129].

The sintering of fly ash resulted in the formation of different phases that impacts the extractability of metals in water, e.g. better leaching was observed for metals like Cr while for other metals, i.e. Cd, Pb, Ni, Cu and Zn the leachability was reduced [137]. The thermal treatment of Al containing fly ash had resulted in the formation of various mixed metal oxides that facilitate the leaching of Al in nitric acid and also the sequential fractional factorial extraction [138]. Zn from fly ash has also been leached by conversion of its non-volatile phases (i.e. hydrozincite, willemite, gahnite) into volatile species (ZnCl₂) at 900 °C; the process is hindered by the presence of S that can be taken care of by using oxygen containing inert gas stream or else alkali chloride salt [139]. The separation of Zn from thermally treated fly ash depends on the competing reactions and mass transfer reactions to the gas stream used in the study as well as on the residence time at heating temperature [135]. Vacuum-assisted high temperature treatment of fly ash carried out at 900 °C and 10 Pa resulted in the effective elimination of Cd 100%, Pb 93.1% and Zn 81.0% within 4 h [140]. Another thermal treatment, i.e. self-propagation high temperature reaction aided by Fe₂O₃-Mg (40:9 w/w), was used for detoxification of Municipal waste incinerator fly ash (MWIFA) at a melting temperature of 1400 °C [141].

Combination of different techniques/sequential extracting techniques

A combination of two techniques was also used by researchers to get better extractability of the heavy metals from fly ash. MSWI fly ash leaching by NaOAc (pH 3) followed by electrolysis using 0.4 A-h of electrical charge resulted in 96.70% Pb and 93.69% Cu recovery. The former process was found to be dependent on L/S ratio, extraction time and metal concentration while current density played an important role in later process efficacy; no impact of pH and temperature was observed [89]. 48 kg high purity Zn was extracted from 1 tonne of fly ash using a three-step procedure consisting of acid extraction, electrolysis using selective reactive extractant (bis(2,4,4-trimethylpentyl) phosphinic acid) and recirculation [142]. *A. niger* extraction of calcined CFA carried out

in presence of quick lime at 900–1000 °C for 12 h resulted in 93.5% removal of Al as compared to 5–8% from uncalcined CFA [93]. High amounts of Al (85%) along with removal of oxides of titanium, iron, silicon, sulphur, phosphorous, sodium and potassium were extracted from fly ash using a sequence of steps consisting of fusion with CaO and coal at 1200 °C; leaching by H₂SO₄ at 80 °C, washing with (NH₄) CO₃, solvent extraction using Primene JMT or di(2-ethylhexyl) phosphoric acid, precipitation with sodium hydroxide and crystallization using ammonium salts [61].

Supercritical fluid extraction combined with the metal ligand extraction technique was able to extract Zn²⁺, Cu²⁺, Pb²⁺, Cd²⁺ and Cr³⁺ from the fly ash. Cyanex 302 (bis(2,4,4-trimethylpentyl)monothiophosphinic acid) was found to be best ligand of all the employed ones that is able to extract 99% Cd and Cu, 87% Pb and 52% Cr when methanol modified CO₂ was used. Independently, Cd²⁺ best extracted with Aliquat 336; D2EHPA (bis(2-ethylhexyl)phosphoric acid) and DiOPA (diisooctylphosphinic acid) is most effective for Zn²⁺ [30].

A rather complicated protocol was observed for gallium recovery from CFA consisting of thermal treatment, HCl leaching, impurity removal and extraction in specially designed reactor using polyurethane foam. As most of the gallium found on the surface of fly ash particles, the process is favoured by smaller particle size, lesser extraction times and increased L/S and hindered by rise in temperature and presence of silica as it results in hindering filtration step and entrapment of gallium, respectively [60].

A series of fly ash treatment and extraction steps consist of spiking with Cu or Cd followed by water leaching; the solid residue was sintered, treated with Cu (or Cd), Ca(OH)₂ and H₃PO₄ and leached in EDTA and TA. The process led to the removal of Na in water leachate, while higher amounts of Ca were extracted in EDTA and that of Cu in TA [143].

Overall analysis

On comparing different techniques, the selection criteria are usually based on the evaluation of factors like energy usage, efficiency of process, process simplicity and liability, cost of the process, potential for reducing the cost and the research progress as pointed out by Tateda [34]. Considering the green nature of process microbial BL is a preferred choice [41] but it is time consuming and costly. When compared chemical leaching under similar experimental conditions, bacterial leaching (*T. thiooxidans*) is found comparable to the H₂SO₄ leaching [45, 54] while fungal BL employing *A. nigar* showed variable results on comparison with independent organic (citric, oxalic and gluconic acids) and inorganic acids (sulphuric and nitric acid) leaching. On the other hand, simulated mixture of organic acids mixed in same ratio as produced during fungal BL step showed poor leaching

potential as compared to fungal BL [47]. But when compared to inorganic leaching, organic acids demonstrate good extractability [74] but are expensive to use. HCl extraction when compared with BL and other processes is shown to be more cost-effective considering its low cost and ease of use [34], but the alkaline nature of the ash led to utilization of large amounts of acid [70]. EDR process has the advantage of being efficient [117] and physically separating the leached metals from the fly ash with help of membrane but use of high energy and fouling of membrane makes the process somewhat unfeasible [121]. Melting or thermal treatment has the advantage of separating heavy metals through evaporation and the resulting metals are pure and hence can be utilized in other metallurgical industries [123], but exceptionally high cost of this process makes it the least favoured process [34].

Conclusion

Fly ash may pose serious risks to the surrounding environment when land filled due to the presence of heavy metals which are highly mobile in nature. Thus, removal of metals is necessary for saviour of life and ecology in soil and aquatic environment. Several techniques were studied in this regard, i.e. bioleaching, chemical leaching, physical leaching, thermal treatment, electrochemical methods and the combination of two or more processes to get better extraction yield and hence detoxification of fly ash. From the literature reviewed, it seems that the selection criteria for a process to be feasible depend highly on the nature of ash and its composition. But overall acid extraction technique followed by metal recovery seems to be an environmentally sound practice prior to the ash disposal if used in combination with water washing pre-treatment.

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