



Journal of Hazardous Materials B136 (2006) 482-501

www.elsevier.com/locate/jhazmat

Review

Environmental-benign utilisation of fly ash as low-cost adsorbents

Shaobin Wang*, Hongwei Wu

Department of Chemical Engineering, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia

Received 8 November 2005; received in revised form 19 January 2006; accepted 19 January 2006 Available online 13 March 2006

Abstract

Fly ash is a waste substance from thermal power plants, steel mills, etc. that is found in abundance in the world. In recent years, utilisation of fly ash has gained much attention in public and industry, which will help reduce the environmental burden and enhance economic benefit. In this paper, the technical feasibility of utilisation of fly ash as a low-cost adsorbent for various adsorption processes for removal of pollutants in air and water systems has been reviewed. Instead of using commercial activated carbon or zeolites, a lot of researches have been conducted using fly ash for adsorption of NO_x, SO_x, organic compounds, and mercury in air, and cations, anions, dyes and other organic matters in waters. It is recognised that fly ash is a promising adsorbent for removal of various pollutants. Chemical treatment of fly ash will make conversion of fly ash into a more efficient adsorbent for gas and water cleaning. Investigations also revealed that unburned carbon component in fly ash plays an important role in adsorption capacity. Directions for future research are also discussed.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Fly ash; Adsorption; Flue gas; Wastewater; Heavy metals; Dye; Organics

Contents

murou		483
Struct	ture of fly ash	483
Adsor	bent for flue gas cleaning	483
3.1.	Sulphur compounds	483
3.2.	NO _x adsorption	485
3.3.	Mercury removal	485
3.4.	Adsorption of gaseous organics	485
Remo	val of toxic metal ions from wastewater	485
4.1.	Adsorption test of various types of heavy metals and metalloids on fly ash	486
4.2.	Adsorption mechanism and kinetics	490
Inorga	anic anions removal from wastewater	491
5.1.	Phosphate removal	491
5.2.	Fluoride adsorption	492
5.3.	Boron adsorption	492
Dye a	dsorption and destruction from water	492
Remo	val of organic compounds from water	495
Leach	ing problem of fly ash in water system	497
Future	e research and perspectives	498
Concl	usion	498
Refer	ences	498
	Struct Adsor 3.1. 3.2. 3.3. 3.4. Remo 4.1. 4.2. Inorga 5.1. 5.2. 5.3. Dye a Remo Leach Futur Concl Refer	Introduction Structure of fly ash . Adsorbent for flue gas cleaning. 3.1. Sulphur compounds. 3.2. NO _x adsorption . 3.3. Mercury removal . 3.4. Adsorption of gaseous organics . Removal of toxic metal ions from wastewater . . 4.1. Adsorption test of various types of heavy metals and metalloids on fly ash . 4.2. Adsorption mechanism and kinetics . Inorganic anions removal from wastewater . 5.1. Phosphate removal . 5.2. Fluoride adsorption . 5.3. Boron adsorption . 5.3. Boron adsorption . 5.3. Boron adsorption . 5.4. Removal of organic compounds from water . Removal of organic mounds from water . . Removal of organic mounds from water . . Removal of organic mounds from water . . Leaching problem of fly ash in water system . . Future research and perspectives . . Conclusion . . References . .

* Corresponding author.

E-mail address: wangshao@vesta.curtin.edu.au (S. Wang).

^{0304-3894/\$ –} see front matter @ 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2006.01.067



Fig. 1. Annual production and sale of fly ash in Australia.

1. Introduction

Since wide scale coal firing for power generation began in the 1920s, many millions of tonnes of ash and related by-products have been created. It is estimated that 349 Mt was produced worldwide in 2000 [1]. While most of produced fly ash is disposal as landfill, which is under pressure for environmental concerns. As a matter of fact, the disposal of fly ash will soon be too costly if not forbidden. Throughout the world, much research is being conducted on the use of waste materials in order to either avert an increasing toxic threat to the environment or to streamline present waste disposal techniques by making them more affordable. It, therefore, follows logically that an economically viable solution to this problem should include utilisation of waste materials in new products for other applications rather than disposal in a landfill.

In Australia, annual production of fly ash (FA) has been steadily increased (Fig. 1), of which about 10% was used, mostly as pozzolan in the building and construction industry [2]. The average percentage of ash as a component of total cement sales has steadily grown over the last 10 years, however, there is a limit to how much fly ash the cement market can take, and development of new market is required. Compared with other countries in fly ash utilisation, Australia has one of the lowest ash utilisation rates and lowest valuable ash utilisation rates [3].

From a power generation perspective, fly ash is a waste, while from a coal utilisation perspective, fly ash is a resource yet to be fully utilised and exploited. The producers of thermal electricity are thus looking for ways to valorise fly ash. Fig. 2 presents the possible uses of fly ash based on the properties of fly ash. Currently, the cement industry might use them as a raw material to produce concrete. The coal fly ash discharged from power plants is also designated as a specified by-product and its use in recycling materials in the fields of agriculture and engineering is widely attempted [4,5]. As one of the effective uses of coal fly ash, its conversion into zeolite has also been widely attempted [6]. Another interesting possibility might be to make it a lowcost adsorbent for gas and water treatment provided production could match industrial needs. A lot of investigations have been reported on using fly ash for adsorption of individual pollutants in an aqueous solution or flue gas. The results obtained when using these particular fly ashes are encouraging for the removal of heavy metals and organics from industrial wastewater. This paper will review the various applications of fly ash as low-cost adsorbents for flue gas cleaning and wastewater treatment for removal of toxic ions and organic matters.

2. Structure of fly ash

The primary components of power station fly ash are silica (SiO_2) , alumina (Al_2O_3) and iron oxides (Fe_2O_3) , with varying amounts of carbon, calcium, magnesium and sulphur. An empirical formula for fly ash based on the dominance of certain key elements has been proposed as [4]:

$Si_{1.0}Al_{0.45}Ca_{0.51}Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.013}Ti_{0.011}.$

Two general classes of fly ash are recognised for coal combustion: Class F normally produced from anthracite, bituminous, or sub-bituminous coals and containing less than 7 wt.% CaO; and Class C normally produced from lignite coals and contains more lime (5–30 wt.%). In general, fly ash has a hydrophilic surface and porous structure. Fig. 3 shows the typical SEM images of fly ash.

3. Adsorbent for flue gas cleaning

3.1. Sulphur compounds

Many industrialised countries are now making efforts to reduce SO_x emissions by installing equipment for flue gas desulphurisation (FGD), and wet-type limestone scrubbing processes are widely employed because of their high $DeSO_x$ efficiency and easy operation. However, these processes have drawbacks



Fig. 2. Possible uses of fly ash considering the natural advantages of this industrial mineral.

such as a large consumption of water and the need for wastewater treatment [5]. Dry-type FGD does not require wastewater treatment but needs a great amount of absorbent compared with wet-type FGD because a high molar ratio of calcium to sulphur is required for obtaining a high $DeSO_x$ efficiency. The reactions are listed as follows:

$$NO + 1/2O_2 \rightarrow NO_2 \tag{1}$$

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$
 (2)

$$Ca(OH)_2 + SO_3 \rightarrow CaSO_4 + H_2O.$$
(3)

Activated carbon has been shown to oxidise reduced sulphur compounds, but in many cases it is too costly for large-scale environmental remediation applications. Coal fly ash can be used as a cheap absorbent for dry-type FGD. A simplified plant view is shown in Fig. 4.

Fly ash recycling in the flue gas desulphurisation process has been shown promising results. Two types of fly ash from fluidised bed (FBC) and pulverised coal combustors (PCC) have been tested as reactive SO₂ sorbents under the treatment of calcium hydroxide [7]. Results showed about 92–100% conversion of CaO to CaSO₄ within 1 h reaction could be achieved with the treated PCC and FBC fly ashes, respectively. Using mixture of fly ash and calcium hydroxide for desulphurisation was also studied by Davini [8,9]. It was proved that using a spray of Ca(OH)₂-fly ash mixtures was an attractive lowcost SO₂ control option. Davini [10] also tested a process using activated carbon derived from fly ash for SO₂ and NO_x adsorption from industrial flue gas. Such a mixture showed



Fig. 3. SEM photos of fly ash (a) Fly ash (b) unburned carbon in fly ash.



Fig. 4. Schematic plant view of flue gas desulfurisation using coal ash [5].

similar characteristics to a typical activated carbon for flue gases.

Apart from direct use of fly ash for FGD, Srinivasan and Gbutzeck [11] explored the synthesis of zeolites from fly ash to adsorption of sulphur dioxide. Breakthrough curves indicated that the zeolites in the samples were able to remove all of the SO₂ in the simulated flue gas for varying periods of time, and that the actual amount of SO₂ removed by the zeolite depended on the type and degree of dryness of the zeolite or zeolite-like material present. In addition, Kastner et al. [12] used coal fly ash with high metal and carbon contents to reduce sulphur compounds for odour removal. Initial results indicated that coal fly ash could catalyse the oxidisation of H₂S and ethanethiol, but not dimethyl sulphide (DMS) and dimethyl disulfide (DMDS) at room temperature. In batch reactor systems and a continuous flow packed bed reactor, removal efficiency for H₂S or ethanethiol could achieve at 99% and 50%, respectively.

3.2. NO_x adsorption

Fly ash was also proposed to be used as an adsorbent for NO_x removal from flue gases [13]. It was found that the unburned carbon remaining in the fly ash particles contributes the main surface area and the adsorption. The unburned carbon could be activated to further improve the adsorption performance. Recently, an adsorption of NO_x using activated chars recovered from fly ash was reported by Rubel et al. [14]. They found that carbon-rich fractions from a gasifier adsorbed one-third of the NO_x compared with a commercial carbon. The CC material was a poor performer for both Hg and NO_x capture.

3.3. Mercury removal

Currently, mercury emissions from coal-fired utility boilers have become a great concern due to the potential environmental threat to human health. Therefore, legislation is setting increasingly strict flue gas emission limits. One promising approach for removing mercury from coal-fired utility flue gas involves the direct injection of mercury sorbents.

A recent study of the Hg emissions from municipal solid waste (MSW) incinerators indicated that, fly ash may promote Hg emission control, when fabric filters were used [15]. The experiments led to the determination of the breakthrough curves for the fixed bed and of the adsorption isotherms at different temperatures in the range of 150–250 °C. Bench-scale and modelling results using fly ash also suggested that certain fly ashes are capable of adsorbing mercury [16]. Malerius and Werther [17] investigated mercury capture in an existing sewage sludge incineration plant. The mercury removal with the fly ash as an adsorbent is simulated and compared with other adsorbents. The adsorption isotherms for the investigated fly ashes were of the Langmuir type whereas for the investigated activated coals and zeolites they were of the Freundlich type.

Serre and Silcox [18] determined whether the unburned carbon that remains in coal fly ash could be used as an inexpensive and effective replacement for activated carbon. Bench-scale tests were conducted at conditions representative of those found in the flue gas trains of coal-fired power plants and municipal waste incinerators. Adsorbed-phase concentrations were as high as 600 ppm. Mathematical models were also developed to simulate the capture of Hg⁰ in flue gas ducts and in baghouses. The results of the simulations indicate that a negligible amount of Hg⁰ can be adsorbed by a dilute suspension of fly ash. The best option for controlling Hg⁰ emissions using fly ash appears to be injection in pulses prior to a baghouse. Meanwhile, the effect of porous structure and surface functionality on the mercury capacity of a fly ash carbon and its activated sample has been investigated. The activated fly ash carbon sample has lower mercury capacity than its precursor fly ash carbon (0.23 mg/g versus 1.85 mg/g), although its surface area is around 15 times larger, 863 m²/g versus $53 \text{ m}^2/\text{g}$. It was found that oxygen functionality and the presence of halogen species on the surface of fly ash carbons may promote mercury adsorption, while the surface area does not seem to have a significant effect on their mercury adsorption capacity [19].

3.4. Adsorption of gaseous organics

Apart from adsorption of NO_x , SO_x and mercury in flue gas, fly ash has also been used for organic gas adsorption. Peloso et al. have investigated the adsorption of toluene vapours on fly ash [20]. Preliminary results showed the possibility of obtaining fly ash products with a satisfactory adsorption performance. Further results showed that a fly ash product, obtained after particle aggregation and thermal activation at a suitable temperature, presented satisfactory adsorption performance for toluene vapours [21]. Another research group determined adsorption kinetics for a representative aromatic hydrocarbon, m-xylene, on three types of fly ash [22]. The results indicated that m-xylene adsorption by fly ash resembled kinetics reported for penetration of absorbates into porous adsorbents. No increase in adsorption rates was observed with increased temperature; rate constants decreased with increase in vapour pressure. This suggested that adsorption was diffusion limited.

4. Removal of toxic metal ions from wastewater

Heavy metals are nowadays among the most important pollutants in source and treated water, and are becoming a severe

Table

public health problem. Heavy metal and metalloid removal from aqueous solutions has been commonly carried out by several processes; chemical precipitation, solvent extraction, ion-exchange, reverse osmosis or adsorption. Among these processes, the adsorption with the selection of a suitable adsorbent can be a simple but effective technique for the removal of heavy metals from wastewater.

4.1. Adsorption test of various types of heavy metals and metalloids on fly ash

Fly ash has been widely explored to be a low-cost adsorbent for heavy metal uptake. Table 1 summarise the results of the important metal ions investigated. Among these metal ions, Pb, Ni, Cr, Cu, Cd, and Hg are the most investigated. The use of fly ash for removal of heavy metals was done as early as in 1975. Gangoli et al. [23] reported an investigation using fly ash for removing heavy metals from industrial wastewaters. Both precipitation and/or adsorption would be involved. Precipitation of the heavy metals results from the presence of calcium hydroxide, while adsorption may be due to the presence of silica and alumina available in the fly ash.

Removal of chromium ions including Cr⁶⁺ and Cr³⁺ using fly ash has been investigated by several groups. For Cr⁶⁺, Grover and Narayanaswamy [24] studied the effects of hexavalent chromium concentrations, fly ash dosage, contact time, and pH on Cr⁶⁺ removal and found that removal was most effective at lower pH values and Cr⁶⁺ concentration. The data fit well in the Freundlich isotherm. Dasmahapatra et al. [25] also investigated the adsorption of Cr⁶⁺ on fly ash. It was observed that the percent removal of Cr⁶⁺ by fly ash is affected by its concentration in aqueous solution, temperature, particle size, and pH. Better separation is obtained at acidic pH and at higher Cr concentration and temperature. Particle size has a non-significant effect on separation. A homogeneous mixture of fly ash and wollastonite (1:1) to remove Cr⁶⁺ from aqueous solutions by adsorption was also reported [26]. The extent of removal is dependent on concentration, pH and temperature of the solution. The amount of adsorption increased with Cr concentration. Maximum removal was observed at pH 2 and 30 °C. The adsorption is first governed by diffusion followed by surface compound formation.

Recently, fly ash from the combustion of poultry litter was assessed as an adsorbent for Cr^{3+} removal from aqueous solution [27]. The adsorption process was studied as a function of temperature and time. Adsorption was best described by the Langmuir model. The adsorption of Cr^{3+} on the fly ash was endothermic and kinetic studies suggested that the overall rate of adsorption was pseudo-second order. At low initial concentrations film diffusion effects contributed to limiting the overall rate of adsorption while at higher initial Cr^{3+} concentrations pore diffusion became more important. An adsorption capacity of 53 mg/g was reached at 20 °C.

Fly ash has also been applied for copper removal. Panday et al. have found that the removal efficiency was dependent on concentration, pH and temperature [28]. The kinetics of adsorption indicated the process to be diffusion controlled and the adsorption was found to be endothermic. The maximum removal is

1			

Summary of adsorption	of metals and metalloids	on fly ash
-----------------------	--------------------------	------------

Metals	Adsorbent	Adsorption (mg/g)	Temperature (°C)	References
Cu ²⁺	Fly ash	1.39	30	[28]
	Fly ash + wollastonite	1.18	30	[28]
	Fly ash	1.7-8.1	-	[34]
	Fly ash(I)	0.34-1.35	20	[38]
	Fly ash	207.3	20	[33]
	Fly ash-washed	207.5	25	[33]
	Fly ash-acid	198.5	25	[33]
	Fly ash	0.63-0.81	25	[29]
	Bagasse fly ash	2.26-2.36	30–50	[42]
	Fly ash	0.76	32	[48]
Pb ²⁺	Fly ash zeolite	70.6	20	[65]
	Fly ash	444.7	25	[33]
	Fly ash-washed	483.4	25	[33]
	Fly ash-aciu	437.0	23	[33]
	Bagasse fly ash	285-566	30-50	[40]
Cd ²⁺	Fly ash	1.6-8.0	_	[34]
	Fly ash zeolite	95.6	20	[65]
	Fly ash	0.67-0.83	20	[37]
	Fly ash(I)	0.08-0.29	20	[39]
	Fly ash(II)	0.0077-0.22	20	[39]
	Fly ash	198.2	25	[33]
	Fly ash-washed	195.2	25	[33]
	Fly ash-acid	180.4	25	[33]
	Bagasse fly ash	1.24-2.0	30-50	[44]
NI;2+	Fly ash	0.05	25 30_60	[01]
111	Fe impregnated fly ash	9-14.0	30-60	[35]
	Al impregnated fly ash	10-15 75	30-60	[35]
	Fly ash(I)	0.40-0.98	20	[38]
	Fly ash(II)	0.06-1.16	20	[38]
	Bagasse fly ash	1.12-1.70	30-50	[44]
Zn ²⁺	Fly ash	6.5-13.3	30-60	[35]
	Fe impregnated fly ash	7.5–15.5	30-60	[35]
	Al impregnated fly ash	7.0–15.4	30-60	[35]
	Fly ash	0.25-2.8	20	[37]
	Fly ash(1)	0.25-1.19	20	[38]
	Fiy asn(11) Bagasse fly ash	0.07 - 1.50 2.34, 2.54	20	[38]
	Bagasse fly ash	13 21	30	[42]
	Fly ash	4.64	23	[60]
	Fly ash	0.27	25	[61]
	Fly ash	0.068-0.75	0-55	[62]
Cr ³⁺	Fly ash	52.6-106.4	20-40	[27]
Cr ⁶⁺	Fly ash + wollastonite	2.92		[26]
	Fly ash + China clay	0.31		[26]
	Fly ash	1.38	30-60	[36]
	Fe impregnated fly ash	1.82	30-60	[36]
	Al impregnated fly ash	1.67	30-60	[36]
	Fly ash(I)	0.33	20	[39]
	Bagasse fly ash	4 25-4 35	30-50	[35]
Hg ²⁺	Fly ash	2.82	30	[30]
8	Fly ash	11.0	30-60	[36]
	Fe impregnated fly ash	12.5	30-60	[36]
	Al impregnated fly ash	13.4	30-60	[36]
	Sulfo-calcic	5.0	30	[53]
	Silico-aluminous ashes	3.2	30	[53]
	Fly ash-C	0.63-0.73	5-21	[31]
As ⁵⁺	Fly ash coal-char	3.7-89.2	25	[66]
As	Fly ash	7.7–27.8	20	[64]
Cat	Fiy ash coal-char	0.02-34.5	20 25	[60]
CS.	r y asn zeonte	443.9	23	[07]

observed at pH 8. Fly ashes with different quantities of carbon and minerals were also used as adsorbents to investigate the contribution of precipitation and adsorption to the removal of aqueous Cu^{2+} [29]. The carbon fraction in fly ash was important in the removal of Cu^{2+} . The specific adsorption capacities of carbon ranged from 2.2 to 2.8 mg Cu/g carbon, while those for mineral were only about 0.63–0.81 mg Cu/g mineral. Consequently, Cu^{2+} removal owing to precipitation increases with a decreasing carbon fraction and the contribution of copper precipitation was estimated to be approximately 23–82% of total removal, depending on the carbon fraction of fly ash.

For mercury adsorption in aqueous solution, fly ash was also found to be effective. Sen and De found coal fly ash presented a comparable adsorption with activated powdered charcoal [30]. Solution pH was the most important parameter affecting the adsorption. The optimum pH range was 3.5–4.5. Kapoor and Viraraghavan reported a similar work [31]. The optimum pH was found to be between 5.0 and 5.5. The adsorption isotherm data were described adequately by both the Langmuir and the Freundlich models. The adsorption process was found to be endothermic.

Papachristou et al. [32] determined the selective adsorption of various metal ions (Na, K, Mg, Ca, Cu, Cd, Mn, Hg, Cr, Pb, and Fe) by two different fly ashes. Experiments indicated that one fly ash sample showed a selectivity in adsorbing heavy metal ions from aquatic systems. Lead ions were found to be selectively adsorbed at a mean value of 19 meq of Pb²⁺ per 100 g of fly ash. This selective adsorption could be attributable to the crystalline ettringite mineral formation after the hydration of the fly ash.

Metallurgical solid wastes, i.e. bauxite waste red muds and coal fly ashes have been used for toxic heavy metals, i.e. Cu^{2+} , Pb^{2+} and Cd^{2+} , removal from water [33]. The breakthrough volumes of the heavy metal solutions have been measured by dynamic column experiments so as to determine the saturation capacities of the sorbents. The investigation showed that fly ash exhibited higher adsorption capacity than red mud. The sorption sequence is Cu>Pb>Cd in accordance with the order of insolubility of the corresponding metal hydroxides. Similar results on adsorption of Cd and Cu by fly ash were also reported from Ayala et al. [34]. Adsorption capacity increases as metal initial concentration decreases. The removal phenomenon appears to be that the fly ash neutralizes the metal solution due to its alkaline nature. The presence of high ionic strength, or appreciable quantities of Ca and Cl ions does not have a significant effect on the adsorption of these metals by fly ash.

Banerjee et al. studied adsorption of several toxic metal ions, Ni²⁺ [35], Zn²⁺ [35], Cr⁶⁺ [36] and Hg²⁺ [36], on fly ash and Al- and Fe-impregnated fly ash. The impregnated fly ash showed much higher levels of adsorption capacity for all ions as compared to untreated fly ash. The adsorption was found to be exothermic for Ni²⁺ and endothermic in case of Zn²⁺ using the values of enthalpy change. The adsorption capacity of FA, Al-FA, and Fe-FA for Cr⁶⁺ was found to be 1.379, 1.820, and 1.667 mg/g and that of Hg²⁺ was 11.00, 12.50, and 13.40 mg/g.

Bayat investigated the removal of Zn^{2+} , Cd^{2+} [37], Ni^{2+} , Cu^{2+} [38], and Cr^{6+} [39] using lignite-based fly ash and activated carbon and found that the fly ash was effective as activated carbon.

The parameters studied include contact time, pH, temperature, initial concentration of the adsorbate, and fly ash dosage. The percent adsorption of Zn^{2+} and Cd^{2+} increased with an increase in concentration of Zn^{2+} and Cd^{2+} , dosage of fly ash and temperature and the maximum adsorption occurred in the pH range of 7.0–7.5. Thermodynamic parameters suggested the endothermic nature of the adsorption process. The effectiveness of fly ash as an adsorbent improved with increasing calcium (CaO) content. Fly ashes were found to have a higher adsorption capacity for the adsorption of Cd^{2+} as compared to Cr^{6+} . Fig. 5 shows the comparison of fly ash and activated carbon in metal adsorption at various pH values.

Gupta research group conducted a series of investigations on fly ash adsorption for heavy metals. They measured the changes in toxicity and heavy metals in a municipal wastewater treatment plant effluent on treatment with fly ash [40]. The effluent after treatment with fly ash for 4 h showed a significant reduction in toxicity, Cu and Pb, PO_4^{3-} and NO_3^{-} contents. Fly ash removed Cu and Pb from the effluent (through adsorption), and the removal of these toxic heavy metals resulted in the reduction of toxicity.

They also use bagasse fly ash from sugar industries for the removal of lead [41], copper and zinc [42,43], cadmium and nickel [44] and chromium [45] from aqueous solutions. Copper and zinc are adsorbed by the developed adsorbent up to 90-95% in batch and column experiments. The adsorption was found to be endothermic in nature and follows both the Langmuir and Freundlich models. For Cd and Ni, the batch test showed 90% removal is possible in about 60 and 80 min, respectively. Maximum adsorption of cadmium and nickel occurred at a concentration of 14 and 12 mg/L and at a pH value of 6.0 and 6.5, respectively. A dose of 10 g/L of adsorbent was sufficient for the optimum removal of both the metal ions. The adsorption data also followed the Langmuir model. The adsorption of both the metal ions increased with increasing temperature indicating endothermic nature of the adsorption process. The removal of Zn is 100% at low concentrations, whereas it is 60-65% at higher concentrations at an optimum pH of 4.0, using 10 g/L of adsorbent in 6-8 h of equilibration time. The uptake decreases with a rise in temperature indicating the process to be exothermic in nature. The removal takes place through film diffusion mechanism at lower concentrations and by particle diffusion at higher concentrations. Lead and chromium are also achieved by the developed adsorbent up to 96-98%. The removal of these two metal ions up to 95-96% was achieved by column experiments at a flow rate of 0.5 mL/min. The adsorption was found to be exothermic in nature.

Pan et al. compared the adsorptive characteristics of the sewage sludge ash (SSA) with fly ash and blast-furnace slag for copper ions [46]. The adsorption test revealed that the adsorption isotherm of SSA for copper ions generally followed the Langmuir model. The removal efficiency was greater than 98% and the estimated maximum capacity of copper adsorbed by SSA was 3.2–4.1 mg/g and close to that of fly ash. The primary mechanisms of copper removal by SSA included electrostatic attraction, surface complex formation, and cation exchange. The precipitation of copper hydroxide occurred only when the



Fig. 5. Effectiveness of an activated carbon-compared to Afsin-Elbistan and Seyitomer fly ashes on the removal of various heavy metals [38].

dosage of SSA and the equilibrium pH of wastewater were at a high level (30–40 g/L and greater than 6.2, respectively).

Rao et al. used raw bagasse and fly ash generated in sugar mills and boilers, respectively, as low-cost adsorbents for the removal of chromium [47], nickel [47], copper [48] and lead [48] from an aqueous solution. The kinetics of adsorption and extent of adsorption at equilibrium are dependent on the physical and chemical characteristics of the adsorbent, adsorbate and experimental system. The efficiencies of adsorbent materials for the removal of Cr^{6+} and Ni^{2+} were found to be between 56.2% and 96.2% and 83.6% and 100%, respectively. These results were obtained at the optimized conditions of pH, contact time, sorbent dose, sorbate concentration of 100 mg/L and with the variation of adsorbent particles size between 0.075 and 4.75 mm. The efficiency of sorption of copper and lead is affected by aqueous solution pH, contact time, adsorbent dose, type and size of adsorbents and initial metal ion concentration. The adsorption capacity follows the sequence of fly-ash > bagasse > PAC for Cu^{2+} removal, and PAC > bagasse > fly-ash for Pb²⁺ removal.

Fly ash has been studied as a pre-filter material for the retention of lead [49]. The results obtained from the retention experiments by the permeameter method indicate that fly ash retains the lead ions through precipitation in the pores as well as onto the surface when the ambient pH value is more than 5.5, and through adsorption when the pH value is less than 5.5. It has been observed that fly ash did not release the retained lead ions when the pH value is between 3.5 and 10.0. Hence, the retention of lead ions by fly ash is likely to be permanent since the pH of most of the municipal landfill leachates are within 3.7–8.8. However, for highly acidic or alkaline leachates, the retained ions can get released.

Ricou et al. studied the removal of Cu, Ni, Zn, Cd and Pb by fly ash and fly ash/lime mixing [50,51]. The experimental results indicate that removal capacity increased with increasing pH. The removal extent was achieved in the order of $Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$. Formation of calcium silicate hydrates (CSH) was supposed to be responsible for increasing removal as also for decreasing desorption.



Fig. 6. Comparison of adsorption capacities obtained by Sodelif and Soprolif fly ashes with mono-metallic solutions and with multi-metallic solutions [52].

Two fluidized-bed sourced fly ashes with different chemical composition, silico-aluminous fly ashes and sulfo-calcic fly ashes, were tested to remove Pb²⁺, Cu²⁺, Cr³⁺, Ni²⁺, Zn²⁺, Cr⁶⁺ [52] and Hg²⁺ [53] from aqueous solutions. The results show that the percentage of adsorbed ions was greater when they were in contact with silico-aluminous fly ashes than sulfo-calcic fly ashes, except in the case of the ion Ni²⁺. The removal of metallic ions increases with increasing pH. However, sulfo-calcic fly ashes remove mercury more efficiently and more steady. Furthermore, removal of mercury was increased with increasing pH. The results showed that mercury is bound to ash surface due to several chemical reactions between mercury and various oxides (silicon, aluminium and calcium silicate) of the surface of the ashes.

Fig. 6 presents a comparison of adsorption capacities obtained from two sets of fly ash samples, Sodelif and Soprolif, when experiments were carried out on mono-metallic and multi-metallic solutions with the same initial concentration of each ion. The values of adsorption capacities are practically identical for these solutions, suggestion no competition exists between the different species of ions adsorbed onto fly ashes, and each metallic ion is adsorbed on specific sites of the surface.

A municipal solid waste (MSW) bottom ash was also used for adsorption of heavy metals, Cu and Ni [54]. The adsorption experiment was conducted using synthetic wastewater and plating rinse water. The adsorption rate increased with decreasing particle size and with increasing liquid/solid ratio; however, the removal efficiency of Cu was higher than that of Ni. In the case of plating rinse water, the adsorption rate decreased sharply at high liquid/solid ratio, and it showed over 80% of adsorption rates for Cu and Ni at an initial pH of 3.

Van Jaarsveld et al. [55] used fly ash as a reactant in creating a geopolymeric matrix for the immobilisation of process water containing 25,000 ppm of Cu or Pb cations. The kinetics of leaching of immobilised metals from the depolymerised fly ash was qualitatively found to proceed along a combination of pore diffusion and boundary layer diffusion control mechanisms. The immobilisation of metals in geopolymerised fly ash proceeds by a combination of physical encapsulation and chemical bonding with adsorption.

Yadava et al. [56] investigated the various rate parameters of Pb^{2+} adsorption on fly ash. The kinetics of Pb^{2+} removal showed

the pore diffusion is mainly rate controlling step. The isosteric heat of adsorption has been determined at different surface coverages of the adsorbent. The negative value of enthalpy change suggests the exothermic nature of the adsorption process.

The removal of cadmium and chromium [57] and copper, nickel and zinc [58] from wastewater by adsorption on fly ash was investigated by Viraraghavan et al. to determine the effects of contact time, pH, and temperature. The alkaline (pH 7-8) aqueous medium favoured the removal of cadmium by fly ash, while chromium removal was maximum in the pH range of 2.0-3.0. The data for the adsorption of cadmium by fly ash fitted well the Langmuir isotherm while the removal of chromium by fly ash followed generally the Freundlich isotherm. The maximum removals of cadmium and chromium by fly ash were 93% and 44%, respectively. For adsorption of copper, nickel and zinc, the effect of contact time, pH, initial concentration of the adsorbate, and temperature on the adsorption process was also studied. Maximum adsorption occurred in the pH range of 3.0–3.5. The Langmuir was found to be applicable to the data of copper, nickel and zinc. Thermodynamic parameters suggested the exothermic nature of the adsorption process.

Vyazova et al. describe the results of a study of the adsorption of a number of heavy metals on fly ash [59]. It is shown that the higher adsorptive capacity is observed in ash samples with a high content of calcium oxide. Coals from different sources were also investigated. It has been found that solutions for coal treatment will affect the adsorption capacity and the adsorption on the coals considered in a sulphuric acid medium proceeds better than in a hydrochloric acid medium.

A process for the treatment of industrial wastewater containing heavy metals, using fly ash adsorption and cement fixation of the metal-laden adsorbent, was investigated by Huang research group [60,61]. Results showed that the fly ash could be an effective metal adsorbent, at least for Zn²⁺ and Cd²⁺ in dilute industrial wastewaters. Fly ash adsorption capacities for Zn²⁺ and Cd²⁺ were 0.27 and 0.05 mg/g, respectively. A 10% metalladen fly ash was tested for leaching and it exhibited metal concentrations lower than the drinking water standards. They further [62] examined the adsorption characteristics of Zn²⁺ onto fly ash. In general, the amount of Zn adsorbed increased as the solid concentration and pH increased, and sharply reached a 99% removal at a specific pH value, then it remained constant over a wide pH region. The fly ash adsorption capacities of Zn ranged from 1.04×10^{-6} to 1.15×10^{-5} mol/g in the pH range of 6.0-7.5. Experimental results indicated that the adsorption was favourable at lower ionic strength, higher pH, and higher temperature and that the adsorption is a physical process enhanced by the electrostatic effect.

Apart from the heavy metals, other metal ions such as As will also cause toxicity to water systems. Several researches have been conducted on their removal using fly ash. The adsorption of As were investigated by some researchers. The effect of various parameters affecting the adsorption of As^{3+} on coal fly ash such as time of equilibration, pH, fly ash dose, etc., has been determined [63]. They found that the fly ash is as good as activated charcoal. The presence of some diverse ions does not affect the adsorption of arsenic adversely. Diamadopoulos et al. present

Table 2
Adsorption capacities of various heavy metals on activated carbon (mg/g) [69]

AC type	Cr ⁶⁺	Cr ³⁺	Pb ²⁺	Zn ²⁺	Cd ²⁺	Ni ²⁺	Cu ²⁺	Hg ²⁺	Li ⁺
PC-Nuchar SA								40.12	
									0.45
GAC-HD400			30						
GAC-C				18					
GAC	6.84			9.90			38		
GAC-F400	145	30			8				
	53.19								
	0.18								
GAC-LB830	0.13								
ACF	40				146	2	9		
Oxidised ACF						10	30		
ACC				2	3.75			65	

work of lignite-based fly ash for removal of As^{5+} from water [64]. The results indicated that the degree of arsenic removal depended markedly on the pH. Removal at pH 4, as demonstrated by the adsorption isotherms, was significantly higher than that at the higher pH values. For 80% removal of arsenic, the solid phase concentration at pH 4 was up to four times greater than that at the other two pH levels. Desorption studies indicated that adsorption of arsenic on fly ash is almost irreversible.

Pattanayak et al. [66] compared the As^{5+} and As^{3+} removal efficiency of a char-carbon (CC), derived from fly ash with those of a commercially available activated carbon (DC) and a carbon produced by arcing of graphite rods (AC). The results indicate that CC and AC adsorbents remove almost equal amounts of As^{5+} at optimum conditions; however, on a percent basis CC removes more As^{3+} than does AC. In comparison, sample DC was found ineffective for the removal of As^{5+} and As^{5+} . The investigation revealed that the adsorption of As^{5+} onto CC is influenced by pH, initial metal concentration and temperature. Higher initial pH will reduce As^{5+} adsorption on CC. The maximum metal uptake was observed in the acidic region around pH 3.

It has been shown that coal fly ash is a good adsorbent for both radionuclides of 137 Cs and 90 Sr [68]. Radiocesium adsorption is maximal around the neutral region whereas radiostrontium adsorption increases with pH, especially above pH 8. Cesium retention sharply drops with ionic strength while strontium adsorption increases sharply and steadily at low and moderate concentrations of the inert electrolyte, respectively. The suggested mechanisms of radionuclide retention by fly ash is specific adsorption of Cs⁺ and irreversible ion-exchange uptake of Sr²⁺.

In addition, fly ash has been converted to zeolites by hydrothermal treatment and used as adsorbent for adsorption of metal ions, radiocesium [67], lead and cadmium [65]. The maximum uptake capacity was estimated to be 3.34 mmol Cs/g, which was 2–3 times higher than those of synthetic zeolite P and natural mordenites. The adsorption capacity for lead and cadmium was estimated to be 70.58 mg lead/g-zeolite and 95.6 mg cadmium/g-zeolite, respectively, when the initial concentration for both ions was 100 mg/L.

Babel and Kurniawan [69] summarise the results of commercial activated carbons, powder (PAC), granular, (GAC), fibrous, (ACF), and clothe (ACC), in heavy metal adsorption (Table 2). Due to the different sources of raw materials, the extent of chemical activation, and the physicochemical characteristics; activated carbons exhibit various adsorption capacities. Comparison between Table 1 and Table 2, it is seen that activated carbon usually exhibits higher adsorption capacity in Cr and Hg ions. While in other cases, fly ash can be more effective than activated carbon.

4.2. Adsorption mechanism and kinetics

For a solid liquid sorption process, the solute transfer is usually characterised by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. The sorption dynamics can be described by the following three consecutive steps which are as follows [70]:

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

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

Various kinetic models have been suggested for adsorption including the Lagergren pseudo-first-order kinetics, the pseudo-second-order kinetics, external diffusion model, and intraparticle diffusion model, which are expressed in Eqs (4)–(7) as listed below:

$$\log(q_{\rm e} - q_t) = \log q_{\rm e} - \frac{k_1}{2.303}t$$
(4)



Fig. 7. Kinetic plots of Cu adsorption on fly ash [28].

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\rm e}^2} + \frac{1}{q_{\rm e}}t$$
(5)

 $\frac{\mathrm{d}C_t}{\mathrm{d}t} = -k_\mathrm{s}S(C_t - C_\mathrm{s})\tag{6}$

$$q_t = k_i(t^{1/2})$$
 (7)

where k_1 , k_2 , k_s and k_i are the pseudo-first order, pseudo-second order rate constant, mass transfer coefficient, and rate parameter of the intraparticle diffusion control stage, respectively, q_e the amount of solute sorbed (mol/g) at equilibrium and q_t the amount of solute on the surface of the sorbent (mol/g) at any time t, C_s and C_t are surface and solution concentration, and S is the specific surface area.

Adsorption kinetics of heavy metals on fly ash has been investigated by several researchers. Most of investigations reported that the metal adsorption usually follows the first-order kinetics [28,35,36,47,71] and that the adsorption is pore diffusion controlled [28,35,36,44,45]. Fig. 7 shows a comparison of kinetic plots for Cu adsorption on a fly ash. A straight line plot of $log(q_e - q_t)$ versus *t* (Fig. 7(A)) suggests the applicability of Lagergren equation, however, the plot of C_t/C_0 versus $t^{0.5}$ (Fig. 7(B)), although linear for a wide range of contact period, do not pass through the origin, indicating that the pore diffusion is the rate controlling step [28].

Kelleher et al. [27] investigated Cr^{3+} adsorption on the fly ash and the kinetic studies suggested that the overall rate of adsorption was pseudo-second order. We have investigated the kinetics of Cu and Ni adsorption on fly ash derived zeolite and the results showed that the adsorption followed the pseudo-secondorder kinetics.

5. Inorganic anions removal from wastewater

Apart from heavy metal ions in wastewater, some other inorganic anions also exist in waters and could be dangerous for human health. Basically, two anions have been much environmental concerns, phosphorous and fluoride. For example, phosphorous loading to surface and groundwater from concentrated agricultural activities including soil fertilisation, feed lots, diaries, and pig and poultry farms is causing water quality problems in rivers, lakes, and estuaries resulting in eutrophication, increased fish mortality and outbreaks of microbes. Because fly ash is enriched with the oxides of aluminium, iron, calcium, and silica, fly ash emerges as candidate material to treat phosphateladen effluents since aluminium, iron and calcium are known to strongly adsorb or precipitate phosphates in many agricultural, industrial and environmental applications.

5.1. Phosphate removal

Kuziemska first reported an investigation using water extract of brown coal fly ash as coagulant for phosphate precipitation in 1980. It was shown that phosphate precipitation occurs immediately after introduction of the coagulant and after a short and intensive mixing due to the very high total alkalinity of extract [72].

The interaction of inorganic orthophosphate at the water/solid interface of four different fly ash samples was investigated by Vordonis et al. [73]. It was found that the uptake of phosphate is extensive on fly ash surfaces and exceeds by far that corresponding to a monolayer coverage. Laboratory phosphorus adsorption experiments were also conducted with regional gravels and alternative adsorptive media including industrial slag and ash by-products. Langmuir and Freundlich isotherms characterised phosphorus adsorption and the maximum adsorption capacity of regional gravels ranged from 25.8 to 47.5 μ g P/g compared to blast-furnace slag 160–420 μ g P/g and fly ash 260 μ g P/g [74].

Ugurlu and Salman investigated the influence of temperature, phosphate concentration, and fly ash dosage on phosphate removal. Phosphate removal in excess of 99% was obtained in these studies. Maximum removals were achieved at 40 °C. The effective removal was due to the high concentration of calcite present in the fly ash. The tests were also carried out on a continuous basis in an adsorption column. The phosphate removal decreased to 80.4% at the end of 72 h. Recently, Grubb et al. [75] carried out batch equilibration experiments using a low calcium, acidic fly ash for phosphate immobilisation on the order of 100-75% for 50 and 100 mg P/L solutions, respectively. A loosely compacted column of fly ash similarly removed 10 mg P/L for over 85 pore volumes. For the amorphous and crystalline phases studied, the immobilisation of phosphate in the fly ash is attributed to the formation of insoluble aluminium and iron phosphates at low to medium values of pH.

Agyei et al. reported a study on the removal of phosphate ion from aqueous solution by fly ash and slag and established that slag removed the solute faster than fly ash. The Frumkin isotherm was found to be the most appropriate equation for constructing adsorption isotherms from the experimental adsorption data [76]. Then, they further compared phosphate ions removal by fly ash, slag, ordinary Portland cement (OPC) and related cement blends. The rate and efficiency of PO_4^{3-} removal were found to increase in the order: fly ash, slag, OPC, apparently mimicking the order of increasing percent CaO in the adsorbents. Blending OPC with fly ash or slag evidently resulted in diminished PO_4^{3-} removal efficiency. Better removal was obtained at higher solute concentration, acidic pH and higher temperature. A first-order kinetic model was used to obtain values for overall sorption rate



Fig. 8. Breakthrough curves for PO_4^{3-} adsorption [77].

constants and intraparticle diffusion constants. For a fixed-bed column (at pH 9.0 and 25 °C), and breakthrough curves (Fig. 8) were constructed to obtain estimated adsorption capacity values of 32, 60, 75, 78 and 83 mg PO_4^{3-} adsorbent for fly ash, slag, OPC + fly ash, OPC + slag and OPC, respectively [77].

5.2. Fluoride adsorption

During the past few years, intensive interest in the problem of excessive fluorides in drinking water is a matter of serious concern around the world, as it causes fluorosis, a disease that affects teeth and bones. Besides the natural geological enrichment of fluoride in ground waters, there can also be formidable contributions from industries. High-fluoride wastewaters can be generated by coal power plants, semiconductor manufacturing, glass and ceramic production, electroplating, rubber and fertilizer manufacturing. Fluoride concentration in industrial effluents is generally higher than that found in natural waters, ranging from tens to thousands of mg/L.

Different technologies have been proposed, tested, and/or applied to remove fluoride from wastewaters. These methods can be divided into two groups: (a) precipitation methods based on the addition of chemicals to the water and (b) sorption methods in which the fluoride is removed by sorption or ion-exchange reactions on some suitable substrate, capable of regeneration and reuse [78]. However, little work has been reported using fly ash for fluoride removal from waters.

Chaturvedi et al. [79] have studied the ability of fly ash to remove fluoride from water and wastewaters at different concentrations, times, temperatures and pH of the solution. The rate constants of adsorption, intraparticle transport, mass transfer coefficients and thermodynamic parameters have been calculated at 30, 40, and 50 °C. The empirical model has been tested at various concentrations for the present system. The removal of fluoride is favourable at low concentration, high temperature and acidic pH. Nemade et al. [80] also carried out batch adsorption studies to determine the fluoride removal efficiency of fly ash, brick powder, wood charcoal, animal charcoal, fish bone charcoal, etc. Based on the efficiency, economy and usage of various low-cost adsorbents specified above, the fish bone charcoal showed a comparatively higher fluoride removal than other adsorbents used.

5.3. Boron adsorption

Boron occurs naturally throughout the environment, and it is commonly found in the oceans. In aqueous solution it is normally present as boric acid and borate ions. Boric acid and boron salts have extensive industrial use in the manufacture of glass and porcelain; in wire drawing; the production of leather, carpets, cosmetics and photographic chemicals; for fireproofing fabrics; and weatherproofing wood. However, few investigations have been reported on boron adsorption using fly ash. Hollis et al. [81] studied the effect of ash particle size, pH, and Ca(OH)₂ presence on the dissolution and adsorption of B by fly ash in aqueous media. A small amount of B was adsorbed by fly ash at pH 7; this was attributed to a ligand exchange mechanism. Sorption of B increased with increasing pH, up to 12, which could not be explained by the coprecipitation with CaCO₃. Ozturk and Kavak [82] investigated adsorption of boron from aqueous solutions using fly ash in batch and column reactors. The effect of parameters such as pH, agitation time, initial boron concentration, temperature, adsorbent dosage and foreign ion on boron removal were observed. Batch adsorbent capacity was calculated as 20.9 mg/g and the capacity value for column study was obtained as 46.2 mg/g.

6. Dye adsorption and destruction from water

Dyes and pigments represent one of the problematic groups; they are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing. Dyes can cause allergic dermatitis, skin irritation, cancer, and mutations. Currently, many methods, such as activated carbon adsorption, chemical oxidation, reverse osmosis, coagulation and flocculation, and biological treatments, have been developed for treating dye-containing wastewater [83]. The adsorption process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Table 3 gives the summary of available data on various dye adsorption capacity on fly ash.

The use of fly ash for the removal of dye from aqueous solution was first reported by Khare et al. [84]. They investigated the effect of different concentrations and pH on victoria blue adsorption and found that adsorption increased with dye concentration and that the maximum removal was achieved at pH 8. The process follows the first-order adsorption rate expression and the uptake of victoria blue by fly ash is diffusion controlled. The equilibrium data fit well in the Langmuir model of adsorption.

Gupta et al. [85] investigated the ability of fly ash to remove Omega Chrome Red ME from aqueous solutions and found that low adsorbate concentration, small particle size of adsorbent, low temperature, and acidic pH of the medium favour the removal of chrome dye. The thermodynamics of chrome dye-fly ash system indicates spontaneous and exothermic nature of the process. The pronounced removal of chrome dye in the acidic range may be due to the association of dye anions with the positively charged surface of the adsorbent. They further investigated the application of a homogeneous mixture of fly ash and coal

Table 3Comparison of dye adsorption on fly ash

Dye	Fly ash type	Adsorption capacity (mol/g)	Temperature ($^{\circ}C$)	Adsorption isotherm	Kinetic model	References
Methylene blue	Coal FA	14.4×10^{-5}	25	Langmuir		[88]
Crystal violet	Coal FA	9.76×10^{-5}	25	Freundlich	Lagergren first-order	[90]
Rosaniline hydrochloride	Coal FA	1.35×10^{-5}	25	Freundlich	Lagergren first-order	[90]
Methylene blue	FA-F	1.89×10^{-5}	22	Langmuir		[91]
Rhodamine B	FA-F	1.15×10^{-5}	22	Langmuir		[91]
Egacid orange II	FA-F	2.364×10^{-4}	22	Langmuir		[91]
Egacid Red G	FA-F	1.405×10^{-4}	22	Langmuir		[91]
Egacid yellow G	FA-F	5.2×10^{-5}	22	Langmuir		[91]
Midlon Black VL	FA-F	3.3×10^{-5}	22	Langmuir		[91]
Acid Blue 29	FA	3.25×10^{-6}	_	Freundlich		[87]
Acid Blue 9	FA	5.43×10^{-6}	-	Freundlich		[87]
Acid Red 91	FA	2.34×10^{-6}	_	Freundlich		[87]
Acid Red 1	FA	7.26×10^{-6}	_	Freundlich		[87]
Congo red	FA-C	4.47×10^{-5}	20	Freundlich	Pseudo-second-order	[93]
Methylene blue	FA-F	3.47×10^{-6}	_	Langmuir		[94]
Methylene blue	FA-F	1.4×10^{-5}	30	Redlich-Peterson		[96]
Methylene blue	FA-HNO ₃	2.2×10^{-5}	30	Redlich-Peterson		[96]

for the removal of Omega Chrome Red ME. The equilibrium data fit well in the Langmuir model of adsorption, showing the formation of monolayer coverage of dye molecules at the outer surface of the adsorbent [86].

Ramakrishna and Viraraghavan [87] reported an investigation on four low-cost adsorbents, peat, steel plant slag, bentonite clay and fly ash, for dye removal. The results showed high removals of acid dyes by fly ash and slag while peat and bentonite exhibited high basic dye removals. For the acid and basic dyes, the removals were comparable with that of granular activated carbon, while for the disperse dyes, the performance was much better than that of granular activated carbon.

Later, they further investigated the effect of fly ash composition and particle size on dye removal capacity. The removal capacity of fly ash for the different dyes was compared with that of granular activated carbon under identical conditions. Lime content in fly ash seemed to influence dye adsorption to a significant degree—better adsorption was observed at lower particle sizes because of the increased external surface area available for adsorption [88].

Gupta et al. [89] utilised bagasse fly ash for the removal of two basic dyes, rhodamine B and methylene blue. Results include the effect of pH, adsorbent dose, dye concentration, and presence of surfactant on the removal of rhodamine B and methylene blue. Rhodamine B is strongly adsorbed at pH 2, whereas methylene blue is strongly adsorbed at pH 8. The percentage of dye removal was higher at high adsorbent concentrations. The presence of anionic surfactant does not affect the uptake of rhodamine B significantly, but will decrease methylene blue adsorption. The adsorption data have been correlated with both Langmuir and Freundlich adsorption models. Thermodynamic parameters obtained indicate the feasibility of the process, and kinetic studies provided the necessary mechanistic information of the removal process.

The use of fly ash as low-cost adsorbent has also been investigated by Mohan et al. [90] for the removal of dyes from wastewater. Adsorption studies were carried out for different temperatures, particle sizes, pHs, and adsorbent doses. The adsorption of each dye was found to increase with increasing temperature, thereby indicating that the process is endothermic in nature. The removal of each dye was found to be inversely proportional to the size of the fly ash particles. The adsorption of each of the cationic dyes increases with increasing pH and adsorbent material. The Langmuir and Freundlich models were employed to fit the adsorption data and the results indicate that the Freundlich adsorption isotherm. Thermodynamic parameters were also evaluated and the negative values of free energy indicate the feasibility and spontaneous nature of the process, and the positive heats of enthalpy suggest the endothermic nature of the process. The adsorptions of crystal violet and basic fuschin follow first-order rate kinetics.

Brown coal fly ashes were tested by Janos et al. [91] as lowcost sorbents for the removal of synthetic dyes from waters. Fig. 9 presents the adsorption isotherms. It was shown that both



Fig. 9. Adsorption isotherm of various dyes on fly ash [91]. △: Egacid Red, □: Midlon Black, ♦: Egacid Yellow, ●: Egacid Orange.

basic (cationic) as well as acid (anionic) dyes could be sorbed onto the fly ash. The adsorption can be described by the multi-site Langmuir isotherm. The sorption capacities were in the range of 10^{-1} to 10^{-3} mmol/g and did not differ significantly for basic and acid dyes. The dye sorption decreased in the presence of organic solvents (methanol, acetone). The presence of oppositely charged surfactants exhibited a pronounced effect on the dye sorption—low concentrations of the surfactant enhanced sorption, whereas high concentrations solubilised the dyes and kept them in solution. Inorganic salts exhibited only a minor effect on the dye sorption. The sorption of basic dyes increased at high pH values, whereas the opposite was true for acid dyes.

Gupta et al. [92] recently used a bottom ash for the toxic textile dye, malachite green, removal. Preliminary information was gathered by batch adsorption studies, which include effect of pH, adsorbent dose, contact time, adsorbate concentration and temperature. It was observed that the maximum uptake of malachite green takes place at a pH of 5.0 and beyond that pH it attains the same maximum value. The results also showed that the adsorption increases with increasing dye concentration and adsorption temperature. Plausible mechanism of the on-going adsorption process and thermodynamic parameters involved were obtained by carrying out kinetic measurements. The data obtained was successfully used to equate Langmuir and Freundlich adsorption isotherm models. A fixed-bed column was designed and necessary parameters were calculated by applying mass transfer kinetic approach. Attempts were also made to recover dye and regenerate the column.

The adsorption of Congo red from solution was carried out using calcium-rich fly ash with different contact times, concentrations, temperatures, and pHs [93]. The adsorption was between 93% and 98% under the conditions studied. Kinetic studies showed that the adsorption process obeyed the pseudo-second-order kinetic model. It was also determined that the adsorption isotherm followed Freundlich and Dubinin-Radushkevich models and that the adsorption was spontaneous and endothermic.

Woolard et al. investigate fly ash modified by hydrothermal treatment with NaOH to hydroxysodalite zeolite. The cation exchange capacity of the modified ash was significantly increased over that of the raw fly ash. Adsorption experiments showed that the modified fly ash adsorbed a cationic dye (methylene blue) to a much greater extent than an anionic dye (alizarin sulphonate). Saturation adsorption revealed that the capacity of the ash for methylene blue had increased 10-fold during modification when compared to the raw ash. Adsorption is thus ascribed to be a surface effect rather than involving incorporation into the channels of the hydroxysodalite structure [94].

Six different fly ashes, in both an untreated and an acidified form, were studied with respect to their ability to remove colour and organic materials [95]. Colour, fluorescence, and chemical oxygen demand were used to monitor the removal. The apparent predominant mechanism varies with the pH and the chemical characteristics of the ash. These mechanisms include carbon sorption, calcium precipitation of tannins and humics, sorption on the fly ash surface by silica, alumina, and/or iron oxide and, in the acidified situation, coagulation of coloured colloids in the



Fig. 10. Relationship between adsorption capacity and carbon content in fly ash [97].

effluent dissolved from the fly ash. Some additional deleterious components are dissolved into the effluent during the treatment process. Many of these materials can, however, be removed by using a two-stage fly ash sorption process. Particularly of interest is the ability to remove over 90% of the boron from the effluent.

Fly ash and treated fly ash by physical and chemical methods have been employed as adsorbents for the removal of a typical basic dye, methylene blue, from aqueous solution [96]. It is found the raw fly ash showed adsorption capacity at 1.4×10^{-5} mol/g and that heat treatment reduces the adsorption capacity but acid treatment by HNO3 results in an increase in adsorption capacity of fly ash $(2.4 \times 10^{-5} \text{ mol/g})$. For fly ash, adsorption of methylene blue is endothermic reaction. Our research also found that adsorption capacity of fly ash is dominantly contributed by the porous unburned carbon in fly ash, rather than the fly ash itself [97]. Fig. 10 presents the relationship between adsorption capacity of methylene blue and crystal violet on FA and the carbon content in FA. As seen that there is a significant linear correlation between carbon content and adsorption capacity. Further investigation show that unburned carbon exhibits much high adsorption capacity than mineral parts of fly ash [98].

All above reports have demonstrated that fly ash could be an effective adsorbent for dye removal, however, few investigations have been conducted in comparison of adsorption performance of fly ash with commercial activated carbon under similar conditions. Ramakrishna and Viraraghavan found that activated carbon exhibited better removal efficiency than fly ash for basic and acid dyes while fly ash showed better performance in removal of dispersed dye [87]. Table 4 lists some results in dye adsorption using activated carbon. From Tables 3 and 4, it is seen that activated carbon usually presents higher adsorption capacity.

In addition, coal fly ash has been used as a heterogeneous catalyst in peroxidative decolonization of aqueous solution of several reactive drimarene dyes using hydrogen peroxide [100]. The effects of various parameters (source of fly ash, fly ash loading, temperature, pH, initial concentration of dye and hydrogen peroxide, and deactivation of catalytic effect of fly ash)

 Table 4

 Adsorption capacity of various activated carbon in dye adsorption [99]

Dye	Adsorbent	Capacity (mol/g)
Basic blue 9	AC from coconut shell	0.52×10^{-4}
Basic blue 9	AC from bamboo	4.48×10^{-4}
Basic blue 9	Natural zeolite	0.45×10^{-4}
Basic violet 10	AC from pistachio shells	$(1.6-1.9) \times 10^{-4}$
Basic violet 10	AC from fertiliser waste	$(1.7-1.9) \times 10^{-4}$
Basic violet 10	AC from rice husk	$(0.7-1.0) \times 10^{-4}$
Basic violet 3	AC from coconut husk	1.67×10^{-4}
Acid blue 40	Activated carbon	2.82×10^{-4}
Acid red 88	Activated carbon	$2.72 imes 10^{-4}$

were studied. It was found that at 60 °C and pH 2.0, only 2% (weight/volume) fly ash loading could completely decolourise 100 mg/L dye solution within 180–1770 s for an initial H_2O_2 concentration of 1500 mg/L, depending on the source of fly ash and dye used.

For the kinetics of dye adsorption on fly ash, few studies have been carried out. It has been found that the adsorption of dye on fly ash can also be described using pseudo first-order and pseudo-second-order kinetics. Mohan et al. [90] investigated the adsorption of two basic dyes on fly ash and the adsorption followed the first-order rate kinetics. While, Acemioglu reported that the adsorption of Congo red on calcium-rich fly ash obeyed the pseudo-second-order kinetic model [93]. Our recent work showed that the pseudo-second-order kinetic model would be better in describing the kinetics of dye adsorption than the firstorder kinetics [101].

Table 5

C	comparison of	of	organic	pol	lutant	adsorp	tion	on	ffy	as	ł
---	---------------	----	---------	-----	--------	--------	------	----	-----	----	---

7. Removal of organic compounds from water

Phenolic compounds are among the most common organic pollutants of wastewater and a lot of work has been done on adsorption of phenolic compounds. Biological treatment, activated carbon adsorption and solvent extraction are the most widely used methods for removing phenols and its derivatives from wastewaters. Recently, fly ash has been showing good adsorption qualities for phenolic compounds. Table 5 presents a summary of adsorption capacity of various organics on fly ash.

Khanna and Malhotra [114] first reported an investigation using fly ash for phenol removal. Their work dealed with kinetics and mechanism of phenol removal of fly ash and provided data useful in the design of phenol-fly ash adsorption systems. Adsorption of phenol and cresol and their mixtures from aqueous solutions on activated carbon and fly ash compared [115]. The effects of contact time and initial solute concentration have been studied and isotherm parameters were evaluated. The Freundlich isotherm has been found to be more suitable for all the systems investigated. Equilibrium experiments were also performed to evaluate the removal efficiency of phenol from water on fly ash. The adsorption experiments were undertaken using fly ash treated at three different pH levels and with three different temperatures. The results indicated that although phenol can be removed from water, this depends markedly on the temperature and pH value of the treatment solution employed [116].

Adsorption isotherms for adsorption of phenol, 3chlorophenol, and 2,4-dichlorophenol from water onto fly ash were determined [102]. These isotherms were modelled by the Freundlich isotherm. The fly ash adsorbed 67, 20, and 22 mg/g

Organic compounds	Adsorbent	Temperature (°C)	Capacity (mg/g)	References
Phenol	FA	20	67	[102]
	Sugar fly ash	30-50	0.47-0.66	[103]
	FA-C	21	0.26	[104]
	Wood FA	25	5.4	[105]
2-Chlorophenol	Coal FA	10–30	0.8-1.0	[106]
-	FA-C	25	98.7	[107]
3-Chlorophenol	FA	20	20	[102]
4-Chlorophenol	FA-C	25	118.6	[107]
2,4-Dichlorophenol	FA	20	22	[102]
-	Coal FA	10–30	1.5–1.7	[106]
2-Nitrophenol	Wood FA	25	143.8	[105]
	FA	30–50	5.80-6.44	[108]
3-Nitrophenol	FA	30–50	6.52-8.06	[108]
4-Nitrophenol	Sugar fly ash	30–50	0.76-1.15	[103]
	Wood FA	25	134.9	[105]
	FA	30–50	7.80–9.68	[108]
Cresol	Coal FA	20-32	85.4–96.4	[109]
<i>m</i> -Cresol	Wood FA	25	34.5	[105]
p-Cresol	Wood FA	25	52.5	[105]
DDD	Sugar FA	30–50	$(7.5-7.7) \times 10^{-3}$	[110]
DDE	Sugar FA	30–50	$(6.5-6.7) \times 10^{-3}$	[110]
Lindane	Bagasse FA	30-50	$(2.4-2.5) \times 10^{-3}$	[111]
Malathion	Bagasse FA	30–50	$(2.0-2.1) \times 10^{-3}$	[111]
Carbofuran	FA	25-50	1.54-1.65	[112]
TCB	FA	25	0.35	[113]
HeCB	FA	25	0.15	[113]

for phenol, chlorophenol, and 2,4-dichlorophenol, respectively, for the highest water phase concentrations used. The isotherms for contaminants studied were unfavourable, indicating that adsorption becomes progressively easier as more solutes are taken up. Phenol displayed a much higher affinity for fly ash than 3-chlorophenol and 2,4-dichlorophenol.

The potential of using dried activated sludge and fly ash as a substitute for activated carbon was examined by Aksu and Yener [117]. The pollutant binding rate and capacity of each biosorbent/adsorbent for the removal of phenol was shown as a function of initial pH and initial phenol concentration. The maximum phenol loading capacity of each sorbent was found to be 91.0 mg/g for dried activated sludge, 27.9 mg/g for fly ash and 108.0 mg/g for granular activated carbon at 100 mg/L initial phenol concentration. The phenol sorption data when applied to the Freundlich, Langmuir and Redlich-Peterson isotherm equations, showed better correlation to the Freundlich model for all the sorbents over the entire concentration range. They further investigated removing of o-chlorophenol and p-chlorophenol [107]. The working sorption pH value was determined as 1.0 and the equilibrium uptake increased with increasing initial monochlorinated phenol concentration up to 500 mg/dm for all the mono-chlorinated phenol-sorbent systems. The results showed that the equilibrium data for all the mono-chlorinated phenolsorbent systems fitted the Redlich-Peterson model best within the concentration range studied.

The adsorption of phenolic compounds on a mixture of bottom and fly ashes has been investigated [105]. Thus, the effect of molecular weight and molecular configuration on the adsorption of phenol (Ph), *m*-cresol (*m*-Cr), *p*-cresol (*p*-Cr), 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) from aqueous solution have been determined. The thermodynamic parameters for the adsorption of 2-NP and 4-NP have been calculated on the basis of Everett's isotherm equation. Batch experiments were conducted to produce isotherms for single-component, two-component and four-component systems. For this purpose, high-performance liquid chromatography was used. It was found that the ultimate capacity of the adsorbent is considerably less than that predicted from summing the single-component data; this has been attributed to increased competition for adsorption sites.

Bagasse fly ash, a waste generated in local sugar industries, has been converted into a low-cost adsorbent. The product so obtained has been characterised and used for the removal of phenol and p-nitrophenol [103]. Investigations included the effect of pH, sorbent dosage, phenol concentration and the effect of surfactants on the uptake of phenol and *p*-nitrophenol. The uptake increases when larger quantities of adsorbent are used. Both phenol and *p*-nitrophenol are strongly adsorbed at low pH values. There is no change in the uptake of phenol and *p*-nitrophenol up to pH 8 and 6, respectively, beyond which a sharp decline in adsorption is observed. The presence of an anionic detergent Manoxol-IB reduces the uptake of phenol and *p*-nitrophenol. The adsorption data follow both Langmuir and Freundlich models. Isotherms have also been used to obtain the thermodynamic parameters of the process. Some experiments have also been performed with a view to recover phenols and have in situ chemical regeneration of the spent carbon column.

Adsorbent prepared from fly ash obtained from a thermal power plant was successfully used to remove cresol from an aqueous solution in a batch reactor [109]. The adsorbent was characterised, and significant removal of cresol was achieved. The adsorption isotherms were evaluated and the effects of system parameters, e.g., stirrer speed and temperature on the adsorption, were studied. A theoretical model was proposed, and it was solved by using a quasi-steady-state approach. The intraparticle diffusivity was evaluated from one set of experimental data and was subsequently used to predict the change in bulk concentration with time for other experimental conditions. The predicted and the experimental results are in close agreement. The performance of the adsorbent prepared was favourably compared with that of commercially available activated carbon.

Fly ash from coal-fired thermal power plants can be used for the removal of 2-chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP) with enthalpy changes of about -3 kcal/mol [106]. The amounts of 2-CP and 2,4-DCP removed are affected by the pH value of the solution. The efficiency of removal improves when the pH value is less than the pK_a values of 2-CP and 2,4-DCP, respectively. The adsorbed amount of chlorophenol by fly ash is also affected by particle diameter, carbon content, and the specific surface area of the ash used in this study. As expected, more adsorption takes place with fly ash of higher carbon content and larger specific surface area. Moreover, the adsorbed amount of chlorophenol is not influenced by the matrix in the wastewater, as shown by studying the removal of 2-CP and 2,4-DCP in wastewater from a synthetic fibre plant. Chlorophenols in the wastewater were also removed efficiently through a fly ash column, with breakthrough times being inversely proportional to flow rates.

Viraraghavan and de Maria Alfaro [104] examined the effectiveness of less expensive adsorbents such as peat, fly ash and bentonite in removing phenol from wastewater by adsorption. Batch studies indicated that the optimum pH for the adsorption of phenol on peat, fly ash and bentonite was between 4.0 to 5.0 at 21 ± 1 °C. The adsorption of phenol on peat and bentonite was described well by the Freundlich isotherm whereas the Langmuir isotherm described the adsorption of phenol on fly ash. Peat, fly ash and bentonite were found to adsorb 46.1%, 41.6%, and 42.5% phenol, respectively, from an initial concentration of approximately 1 mg/L.

Sarkar et al. [118] investigated the kinetic aspects of adsorption of some priority organic pollutants, viz., phenol (hydroxybenzene), *o*-hydroxyphenol (1,2-dihydroxybenzene), *m*-hydroxyphenol (1,3-dihydroxybenzene), and 4-nitrophenol (1-hydroxy-4-nitrobenzene), on fly ash have been studied. The process is found to be of complex nature consisting of both surface adsorption and pore diffusion, the extent being estimated from the diffusion coefficient value. Activation parameter data for the ultimate adsorption as well as the pore diffusion are also evaluated. The data indicate that in the studied solute concentration range, external transport mainly governs the rate-limiting process.

Singh et al. [119,120] investigated the adsorption of 2,4dichlorophenol and tetrachlorocatechol by bagasse fly ash (BFA), rice husk fly ash (RHFA) and activated carbon (AC). The practical applicability of these adsorbents in batch operations and various parameters such as effect of contact time, adsorbent dose, pH of the solutions has been investigated. The removal kinetics of 2,4-dichlorophenol shows first-order rate expression and equilibrium adsorption data suited well for both Langmuir and Freundlich isotherms. Economic evaluation of the adsorbents BFA and RHFA with the AC shows that use of BFA and RHFA will be viable.

They [108] further investigated the potential of fly ash, for removing nitro-substituted phenols, i.e. *o*-nitrophenol, *m*nitrophenol and *p*-nitrophenol. The effect of various factors such as adsorbent particle size, pH, phenol concentration and temperature on the sorption capacity was investigated. The removal of nitro-substituted phenols increased with decreasing adsorbent particle size, pH and increasing concentration and temperature. Langmuir adsorption isotherm constants were calculated and it was shown that the adsorption data for phenols onto fly ash fitted the Langmuir model well. The adsorption of the nitrophenols studied followed the first-order rate kinetics.

Relatively limited information is available regarding the kinetics of sorption of organic compounds from solution onto fly ash. For this reason, Banerjee et al. conducted a detailed study of the kinetics of sorption of o-xylene on fly ash [121]. The effects of solute concentration, particle size of the adsorbent, and temperature on the adsorption rate were investigated. It is found that the uptake rate of o-xylene increases significantly with the increasing initial concentration, and gradually approaches a plateau. The results of this research demonstrate that the adsorption reaction can be approximated to the firstorder reversible kinetics. A significant correlation was observed between the rate of adsorption and the inverse of the square of the particle diameter. An examination of thermodynamic parameters shows that the adsorption of o-xylene by fly ash is an exothermic process and is spontaneous at the temperature investigated. Activation energies for the sorption process ranged between 3.1 and 4.3 kcal/mol. The rate at which o-xylene is adsorbed onto fly ash was found to be controlled by the diffusion process.

Among various organic and inorganic water pollutants, pesticides are very dangerous and harmful because of their toxic and carcinogenic nature. Bagasse fly ash, a waste from the sugar industry, was converted into an effective adsorbent and was used for the removal of DDD [2,2-Bis(4-chlorophenyl)-1,1-dichloroethane] and DDE [2,2-Bis(4-chlorophenyl)-1,1dichloroethane] pesticides from wastewater [110]. The DDD and DDE are removed by the developed adsorbent up to 93% at pH 7.0, with the adsorbent dose of 5 g/L of particle size 200–250 μ m at 30 °C. The removal of these two pesticides was achieved up to 97–98% in column experiments at a flow rate of 0.5 mL/min. The adsorption was found to be exothermic in nature. The bagasse fly ash system has been used for the removal of DDD and DDE from the wastewater. The developed system is very useful, economic, and reproducible.

They also use the bagasse fly ash for the removal of lindane and malathion from wastewater [111]. The optimum contact needed to reach equilibrium was found to be 60 min. Maximum removal takes place at pH 6.0. The removal of the pesticides increases with an increase in adsorbent dose and decreases with adsorbent particle size. The optimum adsorbent dose is 5 g/L of particle size 200–250 μ m. Removal of the two pesticides was achieved up to 97–98% under optimum conditions. The material exhibits good adsorption capacity and follows both Langmuir and Freundlich models. Thermodynamic parameters also indicate the feasibility of the process. The adsorption was found to be exothermic in nature. At lower concentrations, adsorption is controlled by film diffusion, while at higher concentrations, it is controlled by particle diffusion mechanisms. The adsorbent is a very useful and economic product for the removal of lindane and malathion.

Hung [122] conducted the batch shaking adsorption study to determine the potential of fly and volcanic ashes in removing organic pollutants from oxidation pond effluents. Factors affecting organic pollutant removals, such as concentrations and sizes of fly and volcanic ashes, initial pond effluent organic concentrations, washed and unwashed conditions of fly and volcanic ashes, were investigated. The TOC (total organic carbon) removal efficiency varied from 30 to 58 percent. The organic removal efficiency increased with increasing ash concentrations, with decreasing initial pond effluent organic concentrations and with decreasing sizes of ashes.

Adsorption of carbofuran on fly ash was studied by Kumari and Saxena [112] at 25 and 50 °C. The data were analysed in terms of isotherm, Freundlich equation and various thermodynamic parameters. The degree of adsorption of carbofuran was determined and found to be in accordance with the partial molar free energies and K_d values.

Batch studies were carried out to investigate the removal of organic acids by adsorption on fly ash impregnated with hydroxides of Al, Cd, Cu, Fe and Ni [123]. The percentage removals of cinnamic acid, indole-3-acetic acid, beta-naphthaleneacetic acid, beta-naphthoxyacetic acid, oxalic acid and trichloroacetic acid from water were 75%, 63.63%, 100%, 95.25%, 85.71% and 78.26%, respectively. The adsorption data recorded follow the Freundlich adsorption isotherm.

A study on sorption kinetics of PCBs on fly ash was conducted in controlled batch systems [113]. TCB and HeCB are removed at 25 °C by adsorption on fly ash up to 97% at pH 7, with an adsorbent dose of 5 g/L. An examination of the thermodynamic parameters shows that the adsorption of TCB and HeCB by fly ash is a process occurring spontaneously at ambient conditions. Activation energies for the sorption process ranged between 5.6 and 49.1 kJ/mol. It was observed that the rate at which TCB and HeCB are adsorbed onto fly ash showed a diffusion limitation. The uptake rate of TCB and HeCB increases with increasing initial concentration and gradually tends to a constant value. A decrease in the adsorption of TCB and HeCB was observed when interfering ions and other PCB congeners were present. Changing the pH in the aqueous solution from 2 to 10 had no effect on the adsorption process. Overall, fly ash can be used for an efficient removal of PCBs from several aqueous solutions.

8. Leaching problem of fly ash in water system

Utilisation of fly ash in water involves potential leaching of some elements into water and thus causes a problem of secondary environmental pollution. It has been found that the surface layer of fly ash particles probably only microns in thickness, contains a significant amount of readily leachable material which is deposited during cooling after combustion. Elements were divided into two groups on the basis of their concentration dependence upon particle size. Results of the analysis by particle size indicates that the elements Mn, Ba, V, Co, Cr, Ni, Ln, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg and S are usually volatile to a significant extent in the combustion process. Elements Mg, Na, K, Mo, Ce, Rb, Cs and Nb appear to have a smaller fraction volatilised during coal combustion [124].

Many important aspects of the leaching behaviour of fly ash have been covered by a number of researchers and addressed in some reviews [124–127]. Experiments results indicate that leachability of heavy metals from coal fly ashes is relatively low and leaching extent is dependent on the conditions of water system. Trace metal concentration in the leachate depends on fly ash weight/solution, pH, concentration of the elements, temperature, pressure and time. In water, rapid leaching of most of the trace metals (except Cu) takes place from the surface of ash particles in lower pH range; all the trace elements lie within acceptable limits [127].

Therefore, it is suggested that some following measures should be taken before fly ash is use as adsorbent for water treatment:

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

9. Future research and perspectives

It is evident that fly ash as coal combustion residue has a great potential in environmental applications. Fly ash is an interesting alternative to replace activated carbon or zeolites for adsorption either in air or water pollution treatment. However, adsorption performance of fly ash strongly depends on fly ash origin and chemical treatment. Up to date, no industrial scale application has been realised. Economic barriers have to be overcome in terms of high value and high volume utilisation. Raw fly ash usually has low adsorption capacity. Modification by physical and chemical treatment would enhance the adsorption capacity [96], thus enhancing the value for application.

Fly ash contains aluminosilicates and is a potential source for zeolite synthesis. Zeolite has a variety of applications as adsorbents and ion exchangers and exhibits much higher capacity than raw fly ash. Therefore, conversion of fly ash into zeolite would make it a high value and high volume utilisation and should be a good direction for fly ash application. In the past years, some investigations have been reported in hydrothermal conversion of fly ash to different types of zeolites using extracted superannuant solution. Few researches have been success in conversion of bulk fly ash into pure zeolite [6]. Therefore, more research should be directed in this area.

Unburned carbon is an important component of fly ash, whose composition in fly ash varies with combustion efficiency. In fly

ash, unburned carbon contents generally range between 1% and 10%. However, higher content of unburned carbon in fly ash will lead to efficiency loss and poor marketability of the fly ash for cement production. On the other hand, unburned carbon is similar to the precursors for production of premium carbon materials, such as activated carbon. Activated carbon made from unburned carbon has a significant potential cost advantage over other activated carbon. Therefore, separation of unburned carbon from fly ash will be beneficial to fly ash application, either for carbon recycling or mineral fly ash application in cement production and zeolite synthesis. However, few investigations have been currently conducted in utilisation of unburned carbon for production of activated carbon. More efforts should be attempted in this work.

10. Conclusion

Fly ash is produced as a by-product of the burning of fossil fuels for power generation. Landfill of fly ash is current the dominant management strategy, however, it has serious environmental problem. Fly ash can be regarded as a low-cost resource or industrial minerals. It is mainly composed of aluminosilicate and unburned carbon. Investigations have demonstrated that fly ash possesses adsorption capacity for removal of gaseous pollutants in air, inorganic ions and organic compounds in water. Comparison with other adsorbents, fly ash could be effective adsorbent depending on the compositions and treatment. To improve removal efficiencies and adsorption capacities, chemical modifications of fly ash needs to be conducted for its conversion to zeolites. The unburned carbon in fly ash also plays an important role for adsorption. The unburned carbon can be converted to activated carbon, which will enhance the adsorption capacity. Separation of unburned carbon from the minerals can bring benefits for applications of unburned carbon and utilisation of mineral section for cements production and zeolite synthesis.

References

- [1] World Coal Institute, Electricity generated from coal, 2000, http://www.wci-coal.com.
- [2] Ash Development Association of Australia, 2004, http://www.adaa. asn.au/welcome.htm.
- [3] A. Elliot, D.-K. Zhang, Australian coal ash—a valuable resources: current state and future directions, CCSD report, 2003.
- [4] R.S. Iyer, J.A. Scott, Power station fly ash—a review of value-added utilization outside of the construction industry, Resour. Conserv. Recy. 31 (2001) 217–228.
- [5] R. Kikuchi, Application of coal ash to environmental improvement—transformation into zeolite, potassium fertilizer, and FGD absorbent, Resour. Conserv. Recy. 27 (1999) 333–346.
- [6] X. Querol, N. Moreno, J.C. Umana, A. Alastuey, E. Hernandez, A. Lopez-Soler, F. Plana, Synthesis of zeolites from coal fly ash: an overview, Int. J. Coal Geol. 50 (2002) 413–423.
- [7] A. Al-Shawabkeh, H. Matsuda, M. Hasatani, Comparative reactivity of treated FBC- and PCC-fly ash for SO₂ removal, Can. J. Chem. Eng. 73 (1995) 678–685.
- [8] P. Davini, Investigation of flue gas desulphurization by fly ash and calcium hydroxide mixtures, Resour. Conserv. Recy. 15 (1995) 193–201.

- [9] P. Davini, Investigation of the SO₂ adsorption properties of Ca(OH)₂fly ash systems, Fuel 75 (1996) 713–716.
- [10] P. Davini, Flue gas treatment by activated carbon obtained from oilfired fly ash, Carbon 40 (2002) 1973–1979.
- [11] A. Srinivasan, M.W. Gbutzeck, Adsorption of SO₂ by zeolites synthesized from fly ash, Environ. Sci. Technol. 33 (1999) 1464–1469.
- [12] J.R. Kastner, N.D. Melear, K.C. Das, Catalytic oxidation of gaseous reduced sulphur compounds using coal fly ash, J. Hazard. Mater. 95 (2002) 81–90.
- [13] G.Q. Lu, D.D. Do, Adsorption properties of fly ash particles for NO_x removal from flue gases, Fuel Process. Technol. 27 (1991) 95–107.
- [14] A. Rubel, R. Andrews, R. Gonzalez, J. Groppo, T. Robl, Adsorption of Hg and NO_x on coal by-products, Fuel 84 (2005) 911–916.
- [15] D. Karatza, A. Lancia, D. Musmarra, Fly ash capture of mercuric chloride vapors from exhaust combustion gas, Environ. Sci. Technol. 32 (1998) 3999–4004.
- [16] T.R. Carey, C.F. Richardson, R. Chang, F.B. Meserole, M. Rostam-Abadi, S. Chen, Assessing sorbent injection mercury control effectiveness in flue gas streams, Environ. Prog. 19 (2000) 167–174.
- [17] O. Malerius, J. Werther, Modeling the adsorption of mercury in the flue gas of sewage sludge incineration, Chem. Eng. J. 96 (2003) 197–205.
- [18] S.D. Serre, G.D. Silcox, Adsorption of elemental mercury on the residual carbon in coal fly ash, Ind. Eng. Chem. Res. 39 (2000) 1723–1730.
- [19] M.M. Maroto-Valer, Y. Zhang, E.J. Granite, Z. Tang, H.W. Pennline, Effect of porous structure and surface functionality on the mercury capacity of a fly ash carbon and its activated sample, Fuel 84 (2005) 105–108.
- [20] A. Peloso, M. Rovatti, G. Ferraiolo, Fly ash as adsorbent material for toluene vapours, Resour. Conserv. 10 (1983) 211–220.
- [21] M. Rovatti, A. Peloso, G. Ferraiolo, Susceptibility to regeneration of fly ash as an adsorbent material, Resour. Conserv. Recy. 1 (1988) 137–143.
- [22] S.J. Rotenberg, G. Mettzler, J. Poliner, W.E. Bechtold, A.F. Eidson, G.J. Newton, Adsorption kinetics of vapor-phase *m*-xylene on coal fly ash, Environ. Sci. Technol. 25 (1991) 830–935.
- [23] N. Gangoli, D.C. Markey, G. Thodos, Removal of heavy metal ions from aqueous solutions with fly ash, in: Proceedings of the National Conference on Complete Watereuse, May 4–8, 1975, pp. 270–275.
- [24] M. Grover, M.S. Narayanaswamy, Removal of hexavalent chromium by adsorption on flayash, J. Inst. Eng. (India), Part EN: Environ. Eng. Div. 1 (1982) 36–39.
- [25] G.P. Dasmahapatra, T.K. Pal, A.K. Bhadra, B. Bhattacharya, Studies on separation characteristics of hexavalent chromium from aqueous solution by fly ash, Sep. Sci. Technol. 31 (1996) 2001–2009.
- [26] K.K. Panday, G. Prasad, V.N. Singh, Removal of Cr(VI) from aqueous solutions by adsorption on fly ash-wollastonite, J. Chem. Technol. Biotechnol. 34A (1984) 367–374.
- [27] B.P. Kelleher, M.N. O'Callaghan, M.J. Leahy, T.F. O'Dwyer, J.J. Leahy, The use of fly ash from the combustion of poultry litter for the adsorption of chromium(III) from aqueous solution, J. Chem. Technol. Biotechnol. 77 (2002) 1212–1218.
- [28] K.K. Panday, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solutions by fly ash, Water Res. 19 (1985) 869–873.
- [29] C.-J. Lin, J.-E. Chang, Effect of fly ash characteristics on the removal of Cu(II) from aqueous solution, Chemosphere 44 (2001) 1185–1192.
- [30] A.K. Sen, A.K. De, Adsorption of mercury(II) by coal fly ash, Water Res. 21 (1987) 885–888.
- [31] A. Kapoor, T. Viraraghavan, Adsorption of mercury from wastewater by fly ash, Adsorpt. Sci. Technol. 9 (1992) 130–147.
- [32] E. Papachristou, G. Vasilikiotis, C. Alexiades, Selective adsorption of heavy metal cations by using fly ash, in: Proceedings of the First International Symposium on Environmental Technology for Developing Countries, Istanbul, Turkey, 1985.
- [33] R. Apak, E. Tutem, M. Hugul, J. Hizal, Heavy metal cation retention by unconventional sorbents (red muds and fly ashes), Water Res. 32 (1998) 430–440.
- [34] J. Ayala, F. Blanco, P. Garcia, P. Rodriguez, J. Sancho, Asturian fly ash as a heavy metals removal material, Fuel 77 (1998) 1147–1154.

- [35] S.S. Banerjee, R.V. Jayaram, M.V. Joshi, Removal of nickel(II) and zinc(II) from wastewater using fly ash and impregnated fly ash, Sep. Sci. Technol. 38 (2003) 1015–1032.
- [36] S.S. Banerjee, M.V. Joshi, R.V. Jayaram, Removal of Cr(VI) and Hg(II) from aqueous solutions using fly ash and impregnated fly ash, Sep. Sci. Technol. 39 (2004) 1611–1629.
- [37] B. Bayat, Combined removal of zinc (II) and cadmium (II) from aqueous solutions by adsorption onto high-calcium Turkish fly ash, Water Air Soil Pollut. 136 (2002) 69–92.
- [38] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes. I. The case of nickel(II), copper(II) and zinc(II), J. Hazard. Mater. 95 (2002) 251–273.
- [39] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes. II. The case of chromium (VI) and cadmium (II), J. Hazard. Mater. 95 (2002) 275–290.
- [40] G. Gupta, N. Torres, Use of fly ash in reducing toxicity of and heavy metals in wastewater effluent, J. Hazard. Mater. 57 (1998) 243–248.
- [41] V.K. Gupta, D. Mohan, S. Sharma, Removal of lead from wastewater using bagasse fly ash—a sugar industry waste material, Sep. Sci. Technol. 33 (1998) 1331–1343.
- [42] V.K. Gupta, I. Ali, Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater, Sep. Purif. Technol. 18 (2000) 131–140.
- [43] V.K. Gupta, S. Sharma, Removal of zinc from aqueous solutions using bagasse fly ash—a low cost adsorbent, Ind. Eng. Chem. Res. 42 (2003) 6619–6624.
- [44] V.K. Gupta, I. Ali, C.K. Jain, M. Sharma, V.K. Saini, Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste, Water Res. 37 (2003) 4038–4044.
- [45] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using bagasse fly ash—a sugar industry waste, J. Colloid Interface Sci. 271 (2004) 321–328.
- [46] S.-C. Pan, C.-C. Lin, D.-H. Tseng, Reusing sewage sludge ash as adsorbent for copper removal from wastewater, Resour. Conserv. Recy. 39 (2003) 79–90.
- [47] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash, Waste Manag. 22 (2002) 821–830.
- [48] M. Rao, A.V. Parwate, A.G. Bhole, P.A. Kadu, Performance of lowcost adsorbents for the removal of copper and lead, J. Water Supply: Res. Technol.-AQUA 52 (2003) 49–58.
- [49] N.S. Pandian, C. Rajasekhar, A. Sridharan, Fly ash as a pre-filter material for the retention of lead ions, J. Test. Eval. 24 (1996) 181– 186.
- [50] P. Ricou, I. Lecuyer, P. Le Cloirec, Removal of Cu²⁺, Zn²⁺ and Pb²⁺ by adsorption onto fly ash and fly ash/lime mixing, Water Sci. Technol. 39 (1999) 239–247.
- [51] P. Ricou-Hoeffer, I. Lecuyer, P. Le Cloirec, Experimental design methodology applied to adsorption of metallic ions onto fly ash, Water Res. 35 (2001) 965–976.
- [52] S. Rio, A. Delebarre, V. Hequet, P. Le Cloirec, J. Blondin, Metallic ion removal from aqueous solutions by fly ashes: multicomponent studies, J. Chem. Technol. Biotechnol. 77 (2002) 382–388.
- [53] S. Rio, A. Delebarre, Removal of mercury in aqueous solution by fluidized bed plant fly ash, Fuel 82 (2003) 153–159.
- [54] Y.-S. Shim, Y.-K. Kim, S.-H. Kong, S.-W. Rhee, W.-K. Lee, The adsorption characteristics of heavy metals by various particle sizes of MSWI bottom ash, Waste Manag. 23 (2003) 851–857.
- [55] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, L. Lorenzen, Factors affecting the immobilization of metals in geopolymerized flyash, Metall. Mater. Trans. B: Process Metall. Mater. Process. Sci. 29 (1998) 283–291.
- [56] K.P. Yadava, B.S. Tyagi, V.N. Singh, Fly-ash for the treatment of water enriched in lead(II), J. Environ. Sci. Health Part A: Environ. Sci. Eng. 24 (1989) 783–808.
- [57] T. Viraraghavan, G.A.K. Rao, Adsorption of cadmium and chromium from wastewater by flyash, J. Environ. Sci. Health, Part A: Environ. Sci. Eng. 26 (1991) 721–753.

- [58] T. Viraraghavan, M.M. Dronamraju, Use of fly ash in the removal of copper, nickel and zinc from wastewater, Water Pollut. Res. J. Canada 28 (1993) 369–384.
- [59] N.G. Vyazova, V.N. Kryukova, V.P. Latyshev, Adsorption of heavymetal ions by ashes of coals of Irsha-Borodinsky, Ishideisky and Neryungrinsky coalfields, Solid Fuel Chem. 37 (2003) 73–76.
- [60] C.-H. Weng, C.-P. Huang, Removal of trace heavy metals by adsorption onto fly ash, in: Proceedings of the 1990 Specialty Conference, Arlington, VA, USA, Jul 8–Nov 90, 1990.
- [61] C.H. Weng, C.P. Huang, Treatment of metal industrial wastewater by fly ash and cement fixation, J. Environ. Eng. 120 (1994) 1470– 1487.
- [62] C.-H. Weng, C.P. Huang, Adsorption characteristics of Zn(II) from dilute aqueous solution by fly ash, Colloids Surf. A: Physicochem. Eng. Aspects 247 (2004) 137–143.
- [63] A.K. Sen, A.K. De, Adsorption of arsenic on coal fly ash, Indian J. Technol. 25 (1987) 259–261.
- [64] E. Diamadopoulos, S. Ioannidis, G.P. Sakellaropoulos, As(V) removal from aqueous solutions by fly ash, Water Res. 27 (1993) 1773– 1777.
- [65] R. Shawabkeh, A. Al-Harahsheh, M. Hami, A. Khlaifat, Conversion of oil shale ash into zeolite for cadmium and lead removal from wastewater, Fuel 83 (2004) 981–985.
- [66] J. Pattanayak, K. Mondal, S. Mathew, S.B. Lalvani, Parametric evaluation of the removal of As(V) and As(III) by carbon-based adsorbents, Carbon 38 (2000) 589–596.
- [67] H. Mimura, K. Yokota, K. Akiba, Y. Onodera, Alkali hydrothermal synthesis of zeolites from coal fly ash and their uptake properties of cesium ion, J. Nucl. Sci. Technol. 38 (2001) 766–772.
- [68] R. Apak, G. Atun, K. Guclu, E. Tutem, Sorptive removal of cesium-137 and strontium-90 from water by unconventional sorbents. II. Usage of coal fly ash, J. Nucl. Sci. Technol. 33 (1996) 396–402.
- [69] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. 97 (2003) 219–243.
- [70] V. Vadivelan, K.V. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, J. Colloid Interface Sci. 286 (2005) 90–100.
- [71] A. Agrawal, K.K. Sahu, B.D. Pandey, A comparative adsorption study of copper on various industrial solid wastes, AIChE J. 50 (2004) 2430–2438.
- [72] I. Kuziemska, Application of water extract of brown coal fly ash to phosphate precipitation from polluted waters, Water Res. 14 (1980) 1289–1293.
- [73] L. Vordonis, P.G. Koutsoukos, A. Tzannini, A. Lycourghiotis, Uptake of inorganic orthophosphate by Greek fly ashes characterized using various techniques, Colloids Surf. 34 (1988) 55–68.
- [74] R.A. Mann, H.J. Bavor, Phosphorus removal in constructed wetlands using gravel and industrial waste substrata, Water Sci. Technol. 27 (1993) 107–113.
- [75] D.G. Grubb, M.S. Guimaraes, R. Valencia, Phosphate immobilization using an acidic type F fly ash, J. Hazard. Mater. 76 (2000) 217–236.
- [76] N.M. Agyei, C.A. Strydom, J.H. Potgieter, Investigation of phosphate ion adsorption from aqueous solution by fly ash and slag, Cem. Concr. Res. 30 (2000) 823–826.
- [77] N.M. Agyei, C.A. Strydom, J.H. Potgieter, The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends, Cem. Concr. Res. 32 (2002) 1889–1897.
- [78] E.J. Reardon, Y.X. Wang, A limestone reactor for fluoride removal from wastewaters, Environ. Sci. Technol. 34 (2000) 3247–3253.
- [79] A.K. Chaturvedi, K.P. Yadava, K.C. Pathak, V.N. Singh, Defluoridation of water by adsorption of fly ash, Water Air Soil Pollut. 49 (1990) 51–61.
- [80] P.D. Nemade, B.J. Alappat, A.V. Rao, Removal of fluorides from water using low cost adsorbents, Water Sci. Technol.: Water Supply 2 (2002) 311–317.
- [81] J.F. Hollis, R. Keren, M. Gal, Boron release and sorption by fly ash as affected by ph and particle size, J. Environ. Qual. 17 (1988) 181–184.

- [82] N. Ozturk, D. Kavak, Adsorption of boron from aqueous solutions using fly ash: batch and column studies, J. Hazard. Mater. 127 (2005) 81–88.
- [83] P.C. Vandevivere, R. Bianchi, W. Verstraete, Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies, J. Chem. Technol. Biotechnol. 72 (1998) 289–302.
- [84] S.K. Khare, K.K. Panday, R.M. Srivastava, V.N. Singh, Removal of victoria blue from aqueous solution by fly ash, J. Chem. Technol. Biotechnol. 38 (1987) 99–104.
- [85] G.S. Gupta, G. Prasad, K.K. Panday, V.N. Singh, Removal of chrome dye from aqueous solutions by fly ash, Water Air and Soil Pollut. 37 (1988) 13–24.
- [86] G.S. Gupta, G. Prasad, V.N. Singh, Removal of chrome dye from aqueous solutions by mixed adsorbents, fly ash and coal, Water Res. 24 (1990) 45–50.
- [87] K.R. Ramakrishna, T. Viraraghavan, Dye removal using low cost adsorbents, Water Sci. Technol. 36 (1997) 189–196.
- [88] T. Viraraghavan, K.R. Ramakrishna, Fly ash for colour removal from synthetic dye solutions, Water Qual. Res. J. Canada 34 (1999) 505–517.
- [89] V.K. Gupta, D. Mohan, S. Sharma, M. Sharma, Removal of basic dyes (rhodamine B and methylene blue) from aqueous solutions using bagasse fly ash, Sep. Sci. Technol. 35 (2000) 2097–2113.
- [90] D. Mohan, K.P. Singh, G. Singh, K. Kumar, Removal of dyes from wastewater using flyash, a low-cost adsorbent, Ind. Eng. Chem. Res. 41 (2002) 3688–3695.
- [91] P. Janos, H. Buchtova, M. Ryznarova, Sorption of dyes from aqueous solutions onto fly ash, Water Res. 37 (2003) 4938–4944.
- [92] V.K. Gupta, A. Mittal, L. Krishnan, V. Gajbe, Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash, Sep. Purif. Technol. 40 (2004) 87–96.
- [93] B. Acemioglu, Adsorption of Congo red from aqueous solution onto calcium-rich fly ash, J. Colloid Interface Sci. 274 (2004) 371–379.
- [94] C.D. Woolard, J. Strong, C.R. Erasmus, Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams, Appl. Geochem. 17 (2002) 1159–1164.
- [95] M.B. Vandenbusch, N.J. Sell, Fly ash as a sorbent for the removal of biologically resistant organic matter, Resour. Conserv. Recy. 6 (1992) 95–116.
- [96] S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and red mud, Water Res. 39 (2005) 129–138.
- [97] S.B. Wang, Y. Boyjoo, A. Choueib, E. Ng, H.W. Wu, Z.H. Zhu, Role of unburnt carbon in adsorption of dyes on fly ash, J. Chem. Technol. Biotechnol. 80 (2005) 1204–1209.
- [98] S.B. Wang, L. Li, H.W. Wu, Z.H. Zhu, Unburned carbon as a lowcost adsorbent for treatment of methylene blue-containing wastewater, J. Colloid Interface Sci. 292 (2005) 336–343.
- [99] H.W. Wu, E. Ng, D.-K. Zhang, S.B. Wang, Properties of large unburnt char particles in fly ash from pulverised-fuel power stations and implications in beneficial separation and utilisation, in: Proceedings of ICCS&T, CD-ROM, 2005.
- [100] S.K. Chaudhuri, B. Sur, Oxidative decolorization of reactive dye solution using fly ash as catalyst, J. Environ. Eng. 126 (2000) 583–594.
- [101] S.B. Wang, H.T. Li, Dye adsorption on unburned carbon: kinetics and equilibrium, J. Hazard. Mater. 126 (2005) 71–77.
- [102] A. Akgerman, M. Zardkoohi, Adsorption of phenolic compounds on fly ash, J. Chem. Eng. Data 41 (1996) 185–187.
- [103] V.K. Gupta, S. Sharma, I.S. Yadav, D. Mohan, Utilization of bagasse fly ash generated in the sugar industry for the removal and recovery of phenol and *p*-nitrophenol from wastewater, J. Chem. Technol. Biotechnol. 71 (1998) 180–186.
- [104] T. Viraraghavan, F. de Maria Alfaro, Adsorption of phenol from wastewater by peat, fly ash and bentonite, J. Hazard. Mater. 57 (1998) 59–70.
- [105] A.E.-H. Daifullah, H. Gad, Sorption of semi-volatile organic compounds by bottom and fly ashes using HPLC, Adsorpt. Sci. Technol. 16 (1998) 273–283.

- [106] P.-C. Kao, J.-H. Tzeng, T.-L. Huang, Removal of chlorophenols from aqueous solution by fly ash, J. Hazard. Mater. 76 (2000) 237–249.
- [107] Z. Aksu, J. Yener, A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents, Waste Manag. 21 (2001) 695–702.
- [108] B.K. Singh, P.S. Nayak, Sorption equilibrium studies of toxic nitrosubstituted phenols on fly ash, Adsorpt. Sci. Technol. 22 (2004) 295–310.
- [109] B. Dutta, J.K. Basu, S. DasGupta, Removal of cresol from aqueous solution using fly ash as adsorbent: experiments and modeling, Sep. Sci. Technol. 38 (2003) 1345–1360.
- [110] V.K. Gupta, I. Ali, Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste, Water Res. 35 (2001) 33–40.
- [111] V.K. Gupta, C.K. Jain, I. Ali, S. Chandra, S. Agarwal, Removal of lindane and malathion from wastewater using bagasse fly ash—a sugar industry waste, Water Res. 36 (2002) 2483–2490.
- [112] K. Kumari, S.K. Saxena, Adsorption thermodynamics of carbofuran of fly ash, Colloids Surf. 33 (1988) 55–61.
- [113] H. Nollet, M. Roels, P. Lutgen, P. Van Der Meeren, W. Verstraete, Removal of PCBs from wastewater using fly ash, Chemosphere 53 (2003) 655–665.
- [114] P. Khanna, S.K. Malhotra, Kinetics and mechanism of phenol adsorption on flyash, Indian J. Environ. Health 19 (1977) 224–237.
- [115] S. Kumar, S.N. Upadhyay, Y.D. Upadhya, Removal of phenols by adsorption on fly ash, J. Chem. Technol. Biotechnol. 37 (1987) 281–290.
- [116] L.J. Alemany, M.C. Jimenez, M.A. Larrubia, F. Delgado, J.M. Blasco, Removal of phenol from aqueous solution by adsorption on to coal fly ash, Adsorpt. Sci. Technol. 13 (1996) 527–536.
- [117] Z. Aksu, J. Yener, Usage of dried activated sludge and fly ash wastes in phenol biosorption/adsorption: comparison with granular activated

carbon, J. Environ. Sci. Health, Part A: Toxic/Hazard. Substances Environ. Eng. 34 (1999) 1777–1796.

- [118] M. Sarkar, P.K. Acharya, B. Bhattacharya, Modeling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters, J. Colloid Interface Sci. 266 (2003) 28–32.
- [119] A.K. Singh, I.D. Mall, D. Singh, I.M. Mishra, Detoxification of bleach plant effluent using low cost adsorbents: removal of 2,4 dichlorophenol, IPPTA: Q. J. Indian Pulp Paper Tech. Assoc. 13 (2001) 11– 17.
- [120] A.K. Singh, I.D. Mall, D. Singh, B. Prasad, I.M. Mishra, Detoxification using low cost adsorbents-removal of tetrachlorocatechol, IPPTA: Q. J. Indian Pulp Paper Tech. Assoc. 14 (2002) 43–47.
- [121] K. Banerjee, P.N. Cheremisinoff, S.L. Cheng, Adsorption kinetics of *o*-xylene by flyash, Water Res. 31 (1997) 249–261.
- [122] Y.-T. Hung, Batch adsorption of organic pollutants from oxidation pond effluents using fly ashes, Int. J. Environ. Stud. 21 (1983) 261– 270.
- [123] H.S. Rathore, S.K. Sharma, M. Agarwal, Adsorption of some organic acids on fly ash impregnated with hydroxides of Al, Cd, Cu, Fe and Ni, Environ. Pollut., Series B: Chem. Phys. 10 (1985) 249– 260.
- [124] R. Iyer, The surface chemistry of leaching coal fly ash, J. Hazard. Mater. 93 (2002) 321–329.
- [125] R. Mohapatra, J.R. Rao, Some aspects of characterisation, utilisation and environmental effects of fly ash, J. Chem. Technol. Biotechnol. 76 (2001) 9–26.
- [126] L. Reijnders, Disposal, uses and treatments of combustion ashes: a review, Resour. Conserv. Recy. 43 (2005) 313–336.
- [127] B. Prasad, N.N. Banerjee, B.B. Dhar, Environmental assessment of coal ash disposal: a review, J. Sci. Ind. Res. India 55 (1996) 772–780.