



Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent

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ABSTRACT

The purpose of this study was to investigate the possibility of the utilization of coal fly ash as a low cost adsorbent material for the adsorption of heavy metal ions (Zn, Pb, Cd, Mn and Cu) present in the municipal solid waste leachate. Batch experiments were conducted to determine the effect of contact time and fly ash dosage on adsorption of heavy metals. Experimental data were evaluated to find out kinetic characteristics of the adsorption process. The isothermal data could be well described by the Freundlich adsorption model. Kinetic parameters of adsorption such as the pseudo first-order constant, pseudo second-order constant and the intraparticle diffusion rate constant were determined. The fly ash concentration required to achieve maximum heavy metal removal was found to be 2 g/L with the removal efficiencies of 39%, 28%, 74%, 42% and 71% for Cu, Mn, Pb, Zn and Cd respectively. The results of the study demonstrated that the fly ash could be used as an effective low cost adsorbent for the removal of heavy metal ions from municipal solid waste leachate.

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1. Introduction

The crude dumping of municipal solid waste (MSW) encourages breeding of insects and rodents, and causes several health hazards, and migration of leachate into sub surface. The amount of leachate generated, the decomposition, stabilization and extraction of pollutants from the waste matrix depend upon several factors, including waste composition, degree of compaction, and absorptive capacity of the waste [1–3]. In general, leachate is highly contaminated with organic contaminants measured as chemical oxygen demand (COD) and biochemical oxygen demand (BOD), with ammonia, halogenated hydrocarbons and heavy metals [4,5]. Due to migration of leachate, soils have been contaminated with heavy metals such as lead, copper, zinc, manganese, chromium and cadmium and these heavy metals in soils lead to serious problems as they cannot be biodegraded [6]. The main sources of heavy metals in the dumping sites are garden pesticides, pharmaceuticals, photographic chemicals, certain detergents, personal care products, fluorescent tubes, waste oil, batteries, wood treated with dangerous substances, electronic waste, electrical equipments, and paint etc., generated at the household [7].

Heavy metal removal from aqueous solutions has been a focus area of research over the recent years. The removal of heavy

metal is achieved through various techniques such as chemical precipitation, solvent extraction, ion-exchange, reverse osmosis or adsorption [8,9]. Among these processes, the adsorption with the selection of a suitable adsorbent can be an effective technique for the removal of heavy metals from wastewater [10–13]. The commonly used adsorbents are activated carbon, alumina, silica, and ferric oxide, and they generally have high metal adsorption capacity. However, they are expensive and difficult to be separated from the wastewater after use. In the recent years, this has prompted a growing research interest into the production of low cost alternatives to these adsorbents from a range of carbonaceous and mineral precursors [14–16]. Fly ash, one of the most abundant waste materials from the combustion of powdered coal, and its major components make it as a potential material for the adsorption of heavy metal contaminants in water and wastewater [17].

Fly ash has been studied as a potential adsorption material for the treatment of wastewater containing heavy metals [18–21], arsenic compounds [22,23], landfill leachate treatment [24] as well as organic compounds such as phenols and dyes [25–28] showing very good adsorption properties. Majone et al. [29] studied the sorption of Pb, Cd, Ni and Cu from a landfill leachate onto kaolinite in relation to the metal speciation in the liquid phase. Komnitsas et al. [30] conducted laboratory column tests to study the efficiency of lignite fly ash barriers in removing heavy metal ions, such as Fe, Zn, Mn, Ni, Cd, Co, Al and Cu, present in high concentrations in acidic leachates produced in mining and waste disposal sites.

In this paper, the results of the study on the adsorption of heavy metals (Zn, Pb, Cd, Mn, Cr and Cu), total dissolved solids (TDS)

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Table 1
Physical properties of fly ash sample.

Property	Values
pH	7.77
Specific surface area (m ² /g)	0.414
Bulk density (kg/m ³)	2510
Specific gravity	2.51
LOI (%)	4.49
Hydraulic conductivity (cm/s)	1.2×10^{-8}
pH _{ZPC}	6.9

and COD present in the leachate from the open dumping site of municipal solid waste on the fly ash barrier material are reported.

2. Materials and methods

2.1. Fly ash

The fly ash used in the batch experiments was collected from the lignite-burning thermal power plant, Neyveli, Tamilnadu. The pH value of the fly ash sample was determined by mixing 2 g of fly ash with 100 mL of distilled water and recording pH at every 1 h interval for a period of 24 h. The specific surface area of the fly ash is determined by the Brunauer Emmet Teller (BET) method. The surface area is determined using SMART SORB 92/93 surface analyzer. The loss on ignition (LOI) was determined by heating a pre-weighed dry sample (left at 105 °C in an oven and then cooled in desiccators) to 600 °C over a period of 2 h [12] (Table 1).

The point of zero charge (PZC) was determined using the solid addition method [31] viz: a series of 100 mL conical flasks, 45 mL of 0.1 M KNO₃ solution was transferred. The pH₀ values of the solution were roughly adjusted from 2 to 10 by adding either 0.1N HNO₃ or NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO₃ solution. The pH₀ of the solutions were then accurately noted. Fly ash (1 g) was added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta\text{pH} = \text{pH}_0 - \text{pH}_f$) was plotted against the pH₀. The point of intersection of the resulting curve at which pH₀ gave the PZC (Fig. 1).

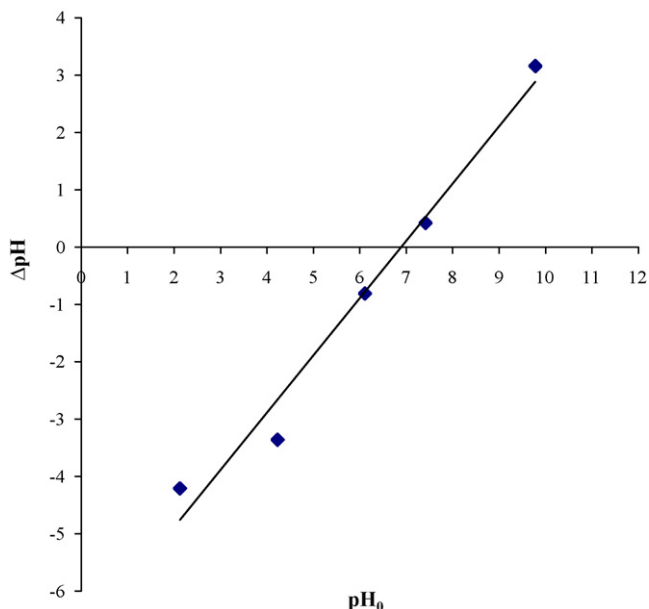


Fig. 1. Point of zero charge (PZC) of the fly ash.

Table 2
Particle size distribution of the fly ash.

Mess (μm)	Weight (%) retained
>45	0
40–45	0
20–40	2.8
10–20	21.2
1–10	53
<1	23

Table 3
Chemical composition of fly ash.

Element oxide	Weight (%)
SiO ₂	36.06
Al ₂ O ₃	15.38
Fe ₂ O ₃	8.28
CaO	34.96
TiO ₂	0.93
K ₂ O	0.12
MgO	2.26
Cu	0.008
Cd	0.0001
Pb	BDL
Mn	<0.001
Zn	0.50
Cr	0.007
Others	1.49

BDL: below detectable limit.

Laser beam techniques were used to determine the particle size of materials both for coarser and finer than 0.045 mm, respectively (Table 2). Elemental analysis was determined by wet chemical method and measurement of elemental concentration was done by using an atomic absorption spectrophotometer (AAS) supplied by PerkinElmer, USA, Model AAnalyst 700 (Table 3). In order to provide a better understanding of the environmental impacts of fly ash utilization, the solubility characteristics of various chemical species associated with fly ash were examined. One gram sample of fly ash was equilibrated with 200 mL of distilled water for 2 h [12]. After filtration, the major chemical constituents in the filtrate were measured (Table 4).

The X-ray diffraction spectrum was obtained by using a Shimadzu XRD 6000 X-ray diffractometer. The prepared fly ash samples were exposed to X-ray ($k = 1.54060 \text{ \AA}$) with the 2θ angle varying between 10° and 80° with Cu K α radiation. The applied voltage and current were 40 kV and 30 mA, respectively. The phases were identified by comparing the peak positions and intensities with those in the JCPDS (Joint Committee on Power Diffraction Standards) data files (Fig. 2). Scanning electron microscopy (SEM) investigations of the fly ash samples were conducted in a JEOL JMT-

Table 4
Soluble concentration of some elements in water from fly ash.

Elements	Concentration (mg/L)	Concentration in (mg/g of fly ash)
Si	3.15	0.63
Al	0.38	0.076
Fe	BDL	BDL
Ca	32	6.4
K	2	0.4
Na	22.1	4.42
Cu	0.009	0.0018
Mn	0.017	0.0034
Zn	0.008	0.0016
Cr	BDL	BDL
Cd	0.003	0.0006
Pb	0.002	0.0004
Ni	BDL	BDL

BDL: below detectable limit.

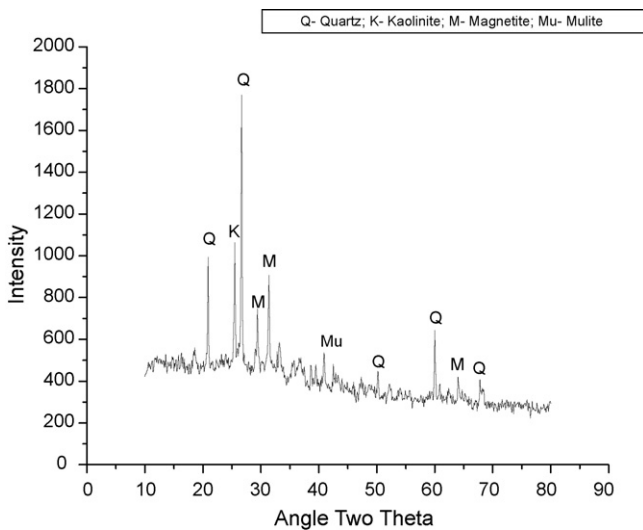


Fig. 2. XRD pattern of the raw fly ash.

300 operated at 30 kV and linked with an energy dispersive X-ray spectrometry (EDXS) attachment. The SEM analysis was done at 1000 \times magnification (Fig. 3). Fourier transform infra red (FTIR) spectroscopic techniques were utilized to identify their functional groups of adsorbent before and after the adsorption. FTIR spectra of the samples were also recorded (Fig. 4) on PerkinElmer Model – System 2000 using KBr pellet method.

2.2. Study area

Chennai, the capital city of Tamilnadu is the commercial and business hub for South India with population of nearly 5 million located on the South East coast of India (Latitude 13 $^{\circ}$ 00'N, Longitude 80 $^{\circ}$ 16'30"E). The estimated municipal solid waste generation in Chennai city is about 3400 tons/day. The city wastes are disposed into two dumping yards namely Kodungaiyur and Perungudi, both incidentally located on wetland areas. The corporation dumps approximately 1750 tons/day of MSW in Kodungaiyur dumping ground, and another 1650 tons/day of MSW in Perungudi dumping ground. The leachate samples used for the batch experiments were

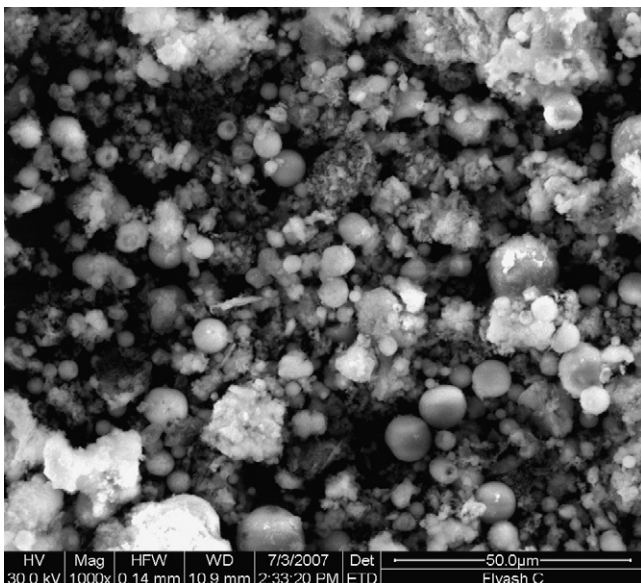


Fig. 3. Micro morphology of raw fly ash (1000 \times).

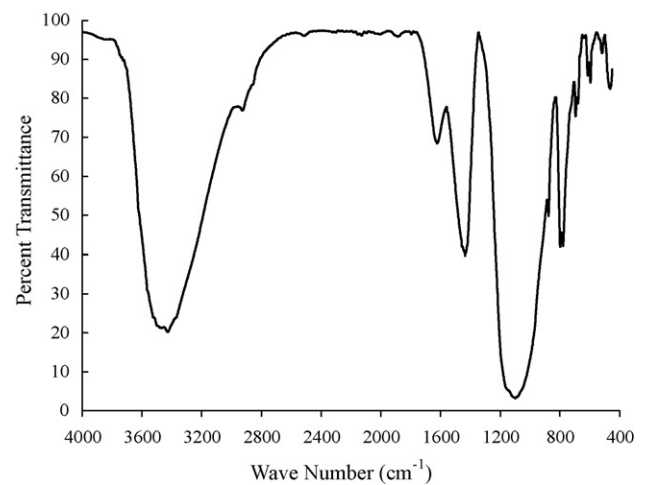


Fig. 4. FTIR spectrum of raw fly ash.

collected from actual leachate streams in the Perungudi dumping site and analyzed for various physico-chemical characteristics and heavy metal concentrations. The characteristics of leachate used for the batch sorption tests are given in Table 5.

2.3. Sorption experiments

The batch sorption studies were carried out by shaking a series of bottles containing different amounts of fly ash dosage (0.1, 0.2, 0.3, 0.4, 0.6 and 0.8 g) in 200 mL of leachate samples collected from the dumping site. Fly ash particles were dried at 110 $^{\circ}$ C for 2 h before the batch experiment. The samples were stirred at room temperature at 150 rpm for 3 h, and their content was then centrifuged at 6000 rpm for 5 min and the supernatant liquid was analyzed for heavy metals concentration, TDS and COD. The leachate samples containing the different dosages of fly ash were shaken for various times to determine the changes of pH with respect to time.

Kinetic study was conducted with the known dosage of adsorbent (0.4 g of fly ash) for the 200 mL of leachate samples. The samples were shaken at an agitation rate of 150 rpm. The samples were taken out at 15, 30, 60, 120, 180, 300, 540 and 720 min. The sorbent solution mixtures were then centrifuged at 6000 rpm for 5 min and the supernatant was analyzed for the metal concentration, TDS and COD. After the removal of heavy metals was completed, the fly ash samples were separated by filtering and dried at 120 $^{\circ}$ C in an oven. Both SEM and FTIR analyses were carried out on the dried fly ash samples to find out modifications in the morphology and functional groups.

Table 5

Characteristics of leachate used for the batch sorption test.

S. no.	Parameters	Concentration
1.	pH	8.03
2.	TDS	18400
3.	EC (μ mho/cm)	28500
4.	COD	4480
5.	Mn	0.151
6.	Cu	0.258
7.	Zn	0.143
8.	Cd	0.250
9.	Pb	0.204
10.	Cr	BDL

All parameters are expressed in mg/L except pH and EC.

3. Results and discussion

3.1. Characterization of adsorbent before adsorption

From Table 1, it can be seen that the BET/N₂ specific surface area of the selected fly ash is 0.414 m²/g. The carbon concentration determined by loss on ignition is found to be less than 5% for the fly ash particles. Table 2 presents the particle distribution of fly ash. It may be noted from Table 2 that approximately 97.2% by weight of the fly ash was less than 20 μm. From Table 3, it can be observed that the SiO₂, Al₂O₃ and Fe₂O₃ contents make up about 60% of the fly ash, while CaO contributed to about 35%. According to the ASTM C618 [32], this fly ash can be classified as class C for having CaO content ranging from 20% to 40%. The results showed that the main components of the fly ash material are silicon, aluminium, calcium and iron compounds. The heavy metals such as Cd, Cr, Pb, Zn, Mn and Cu constitute small portion when compared to the other oxides, as evident from the fly ash samples. According to the results presented in Table 4, the fly ash can be characterized as a non-hazardous solid waste. In addition, the results showed that there is very less probability of leaching of main constituent metals from the fly ash except possibly for the calcium.

The results of the zero point of charge of the fly ash (pH_{PZC} 6.9) is presented in Fig. 1. This shows that at pH less than 6.9 the surface of the fly ash is predominated by positive charges while at pH greater than 6.9 the surface is predominated by negative charges. From Fig. 2, it can be seen that the fly ash is quite rich in quartz, and the other mineral phases present are magnetite, mullite and kaolinite. Quartz and mullite were produced during the thermal decomposition of clay minerals such as kaolinite during combustion. Fig. 3 shows the scanning electron microscope (SEM) image of the raw fly ash. Small tiny spherical particles along with some agglomerates of particles are observed in the image.

The FTIR spectrum (Fig. 4) shows a strong broad band at 3424 cm⁻¹ which indicates the presence of hydroxyl groups on the fly ash [33]. Sharp medium intensity peaks between 1436 and 1620 cm⁻¹ is due to C=O and CH₃ groups present in the clay material of fly ash [34]. A sharp peak at 875 cm⁻¹ is due to the presence of Al atoms in the tetrahedral forms of silica frame work [35]. The band appearing at 780–790 cm⁻¹ corresponds to the quartz present in the fly ash. The double band at 798–780 cm⁻¹, and the bands at 694, 516 and 462 cm⁻¹, could be assigned to quartz as the crystalline

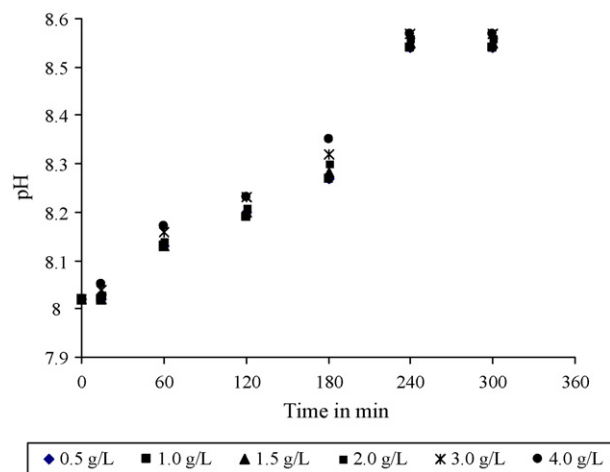


Fig. 6. Variation of pH with different dose of fly ash.

phase in the ash. The band appearing at 1099 cm⁻¹ is associated with T–O (T = Al, Si) asymmetric stretching vibrations. The intensity of the band at 462 cm⁻¹, associated in all cases with T–O bending vibrations, is unrelated to the degree of crystallization of the material. The band associated with tetrahedral aluminium was appeared between 830 and 920 cm⁻¹. The bands appearing between 800 and 500 cm⁻¹ are associated with the tetrahedral vibrations formed by what are known as secondary building units (SBU) and fragments of the aluminosilicate system. These bands are typical characteristic of the double or single rings (depending on the structure of the material) and/or the TO₄ (T = Si, Al) tetrahedral bonds [35].

3.2. Leachate characteristics

The physico-chemical characteristics of the leachate sample analyzed are shown in Table 5. From the values reported in Table 5, it can be concluded that the leachate contains heavy metals such as Pb, Cu, Zn, Mn and Cd. The Chromium concentration was observed to be below detectable limit. The pH was observed in the alkaline range (8.03). This indicates that the methanogenic phase of the leachate. Also the leachate depicts a value of 4480 mg/L for COD.

3.3. Effect of mass of adsorbent on heavy metal removal

The effect of adsorbent dosage on heavy metal removal was analyzed by varying the dosage of fly ash and the results are shown in Fig. 5. From Fig. 5, it can be observed that the removal efficiency increases with the increase in fly ash dose from 0.5 up to 2 g/L for all the heavy metals and remains almost constant thereafter. This is mainly due to the saturation of the adsorbent sites by the adsorption of the metal ions at the dosage level of 2 g/L. Thus it can be concluded that the optimum dose for heavy metals removal is 2 g/L with the removal efficiency of 39%, 28%, 74%, 42% and 71% for Cu, Mn, Pb, Zn and Cd respectively. The removal efficiency of 5.5% and 28% were observed for TDS and COD for the optimum dose of 2 g/L.

3.4. Effect of mass of adsorbent on leachate pH

The effect of fly ash concentration on the pH of the leachate sample was investigated with a wide range of fly ash dosage varied from 0.5 to 4 g/L and the results are shown in Fig. 6. From Fig. 6, it can be observed that the pH of the solution increases rapidly at the beginning with the increase in shaking time and the pH value remains constant after 240 min. The final pH of the leachate sample for the fly ash dosage of 0.5–4 g/L varies from 8.54 to 8.57. The difference between initial and final pH of the leachate sample was found to

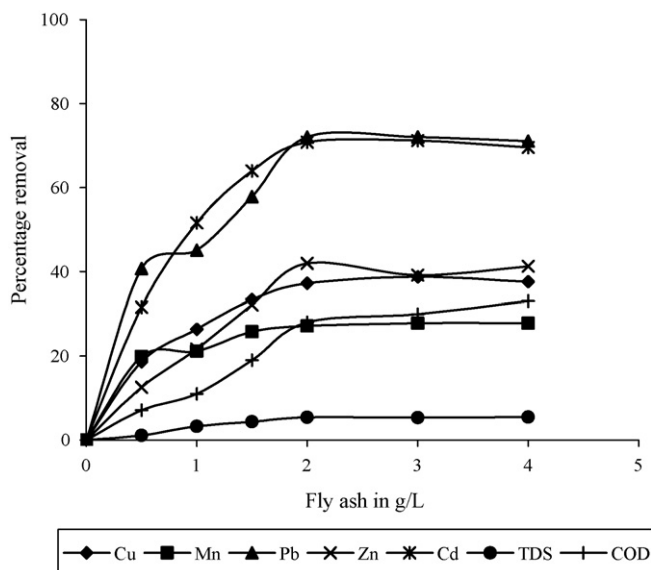


Fig. 5. Effect of mass of adsorbent.

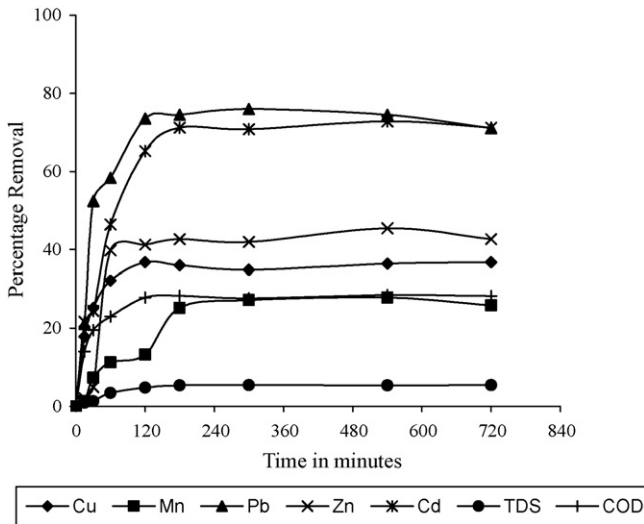


Fig. 7. Kinetics of heavy metal adsorption onto fly ash.

be very minimal (0.53), which is mainly due to the high buffering capacity of the leachate.

3.5. Effect of contact time

Metal ion uptake capacities were determined as a function of time to determine an optimum contact time for the adsorption of heavy metal ions on fly ash. The amount of each compound adsorbed onto the fly ash was calculated by the difference between the content of the compound in the influent solution and that of the effluent solution, corrected with the blank, and it is expressed in percentage.

The variation of percentage of adsorbed substances with respect to time is shown in Fig. 7. From Fig. 7, it can be concluded that the removal of metal ions or the adsorption is increasing with increase in the contact time. Initially the adsorption was low but increases with time quickly. The metal removal in the first 60 min was 58% and 46% for lead and cadmium respectively, while it was 40%, 32% and 11% for zinc, copper and manganese respectively. The optimum time required for the fly ash to get the maximum removal efficiency was found to be 120 min for Pb and Cu, 180 min for Zn, Cd and Mn. At equilibrium, 74% of the lead, 71% of the cadmium, 43% of zinc, and 36% Copper were removed from the leachate. However, only 27% of the Manganese was removed at equilibrium, indicating that more fly ash was needed to remove manganese ions. In addition to the heavy metals removal, 5.4% TDS and 28% COD were also removed from the leachate and attained the equilibrium at 120 min.

3.6. Adsorption isotherm

Two important adsorption isotherms, namely Langmuir [36] and Freundlich [37] were tested for fitting the experimental data. It is found that when compared to the Langmuir isotherm, the Freundlich isotherm plot resulted in a good fit with experimental data as evidenced in Fig. 8. The Freundlich isotherm constants are given in Table 6, and it can be observed that the linear correlation coefficients for all heavy metals of the plots are good. From the isotherm plot shown in Fig. 8, it can be concluded that the Freundlich isotherm was fitting well for the adsorption of heavy metals on fly ash. The 'n' values of Pb and Cd were observed to be very close to the value of 1, thus indicating that the adsorption is favourable for these two heavy metals when compared with other heavy metals such as Zn, Mn and Cu.

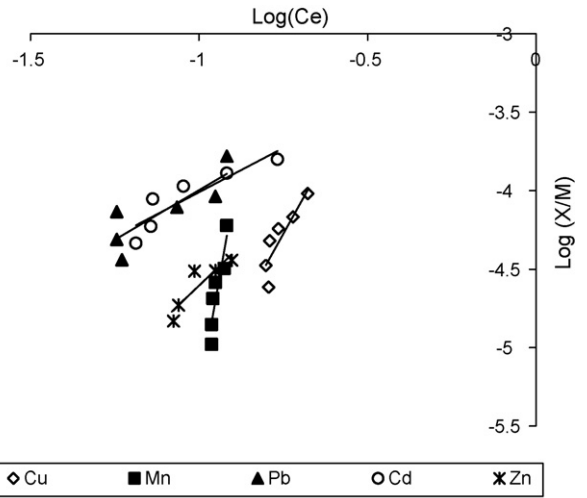


Fig. 8. Freundlich isotherm plot for heavy metals.

Fig. 9 shows the experimental sorption isotherms in terms of metal concentration in the solid phase as a function of equilibrium metal concentration in the leachate. Linear isotherm (Fig. 9) from batch experimental study depicted an upward concavity, which may be due to the presence of precipitation of heavy metals [29]. The occurrence of this type of isotherm curve could be attributed to the presence of co-operative absorption or to the presence of competitive effects of other solutes [38,39].

3.7. Adsorption kinetics

It is known that adsorption process could be controlled with different kinds of mechanisms, like mass transfer, diffusion control, chemical reactions and particle diffusion. In order to clarify the adsorption process, several adsorption models were applied to

Table 6
Freundlich isotherm constants.

Heavy metals	K_F	n	R^2
Cu	0.042865	0.258	0.779
Mn	7828887	0.082	0.831
Pb	0.001863	0.789	0.706
Cd	0.001308	0.888	0.805
Zn	0.002782	0.488	0.814

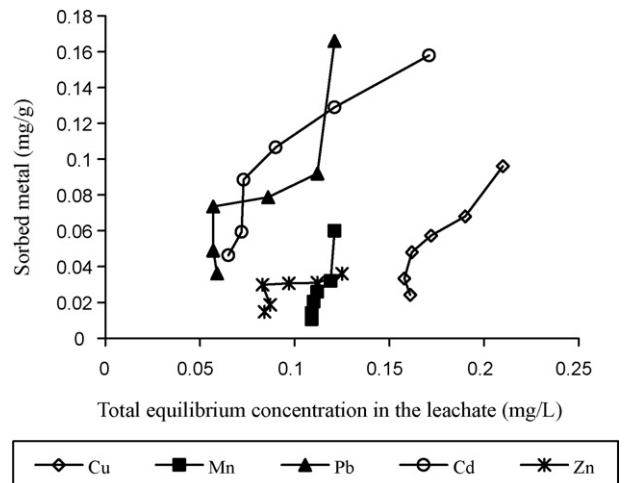


Fig. 9. Adsorption isotherms for combined heavy metals on fly ash.

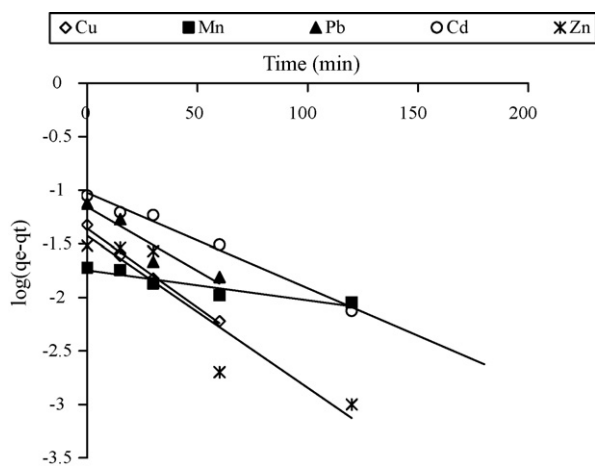


Fig. 10. Fitness of pseudo first-order model.

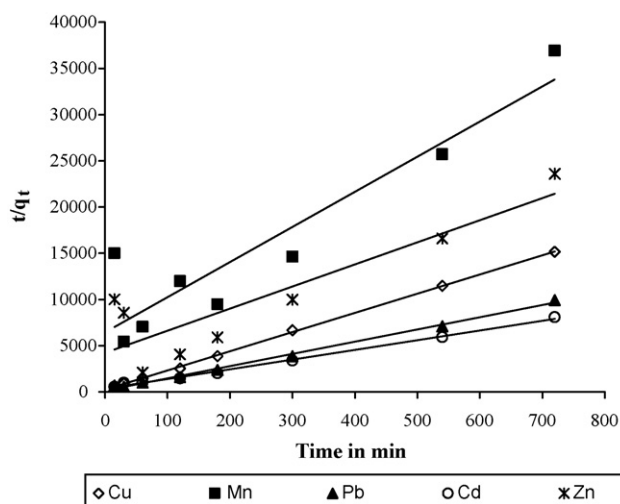


Fig. 11. Fitness of pseudo second-order model.

evaluate the experimental data. For this purpose, Lagergren's pseudo first-order kinetic model, pseudo second-order kinetic model, and intraparticle diffusion model [40] were considered and fitted with the experimental data. Figs. 10–12 show the plot of the first-order, second-order and intraparticle diffusion models for adsorption of heavy metals by the fly ash respectively. Experimental and theoretically calculated adsorption capacities at equilibrium (q_e) values and coefficients related to kinetic plots are listed in Table 7.

It can be seen from the results listed in Table 7 that the linear correlation coefficients for first-order, except for Cu are not good when compared to the second-order model. Thus, these results suggest that the adsorption of Cu, Mn, Pb, Cd and Zn metal ions on fly ash is not pertaining to first-order reaction. It is evident from the results of

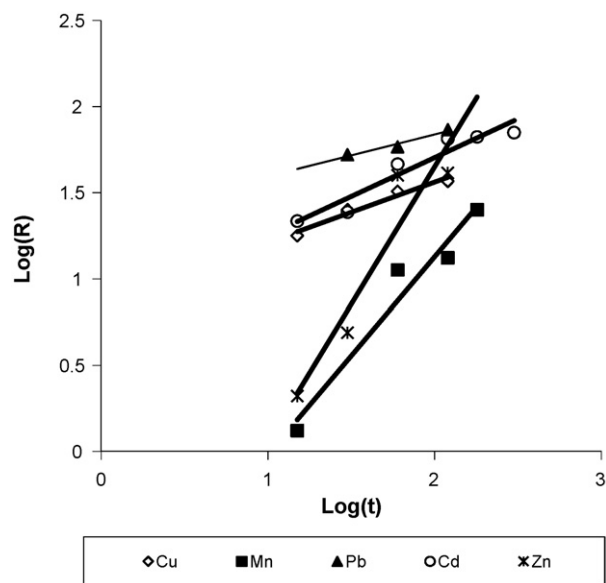


Fig. 12. Fitness of intraparticle diffusion model.

second-order model that the correlation coefficients for Cu, Pb and Cd are very high and the experimental and theoretical q_e values are in good match. On the other hand, for Mn and Zn, the second-order model resulted in poor fit. These results suggest that the adsorption of the metal ions (Cu, Pb and Cd) on fly ash follows the second-order type kinetic reaction based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate, and provides the best correlation of the data [41].

From Table 7, it can be seen that the correlation coefficients (R^2) of Mn and Zn for the intraparticle diffusion model are higher than those for the pseudo first-order and pseudo second-order kinetic models. Higher values of the intraparticle diffusion rate constant ' K_{id} ' illustrate an enhancement in the rate of adsorption, whereas larger values of the gradient of linear plots (α) illustrate a better adsorption mechanism [42]. The values of ' α ' for Pb, Cu and Cd were 0.243, 0.349 and 0.451 respectively. The value of ' α ' being less than 0.50 indicates that the intraparticle diffusion is not a rate-determining step [42]. The value of ' α ' for the Mn and Zn exceeds the value 0.5 indicating that the rate limiting step may be intraparticle diffusion.

3.8. Distribution coefficient

Distribution coefficients (K_d) represent the adsorption affinity of the metallic cations in solution for the solid phase and they could be used to evaluate the mobility and retention of the metallic cations in fly ash. The distribution coefficients for different metal ions were estimated from the metal adsorption at the equilibrium time and the selectivity sequences of the heavy metals on fly ash are given

Table 7
Adsorption kinetic model rate constants for heavy metals.

Heavy metal	q_e (exp) ($\mu\text{g/g}$)	Pseudo first-order			Pseudo second-order			Intraparticle diffusion model		
		q_e (cal) ($\mu\text{g/g}$)	Rate constant k_1 (min^{-1})	R^2	q_e (cal) ($\mu\text{g/g}$)	Rate constant k_2 (g/mg/min)	R^2	K_{id} ($\%/min$)	α	R^2
Cu	48	43.78	0.034	0.993	48.11	1.831	0.999	7.298	0.349	0.960
Mn	20	17.96	0.006	0.881	26.33	0.479	0.862	0.069	1.144	0.950
Pb	75	69.95	0.027	0.896	75.77	1.151	0.996	22.428	0.243	0.960
Cd	89	94.43	0.020	0.986	95.32	0.307	0.996	6.317	0.451	0.920
Zn	31	37.49	0.033	0.861	41.90	5.585	0.773	0.029	1.591	0.900

Table 8Distribution coefficients (K_d) and selectivity sequences.

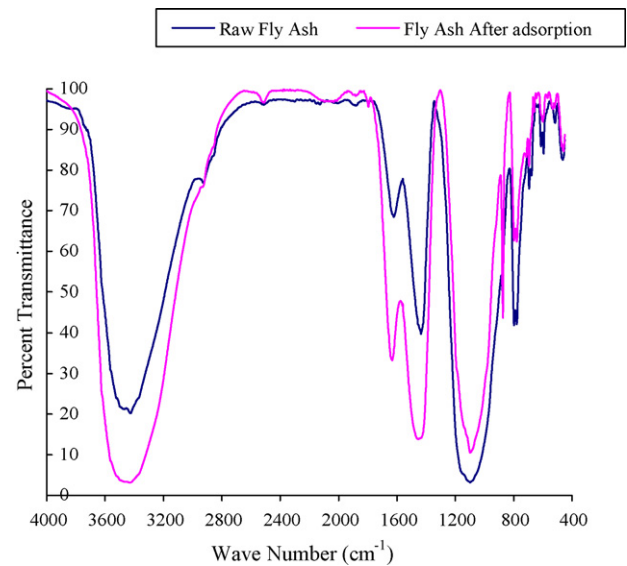
Heavy metal	X/M (mg/g)	C_e (mg/L)	K_d (L/g)	Selectivity sequences
Cu	0.048	0.163	0.294	Pb > Cd > Zn > Cu > Mn
Mn	0.019	0.113	0.168	
Pb	0.075	0.054	1.389	
Cd	0.089	0.072	1.236	
Zn	0.031	0.082	0.378	

in Table 8. The distribution coefficient was found to increase in the order of Mn < Cu < Zn < Cd < Pb. Therefore, it can be concluded that the relative tendency for different metals to bind to them increases in the same order. The K_d of adsorption of Mn, Cu and Zn are very low when compared with that of the Pb and Cd. The high values of K_d proved that the metal is retained mostly by the solid phase through adsorption reactions [43], whereas low values revealed that the major proportion remains soluble in the leachate solution [44]. Those results demonstrated that adsorption of metal ions followed in the descending order of $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Mn^{2+}$. The sorption of Pb on fly ash was higher than that of the other metals and this behaviour could be attributed to the larger ionic radius and higher electro negativity of Pb [33,45].

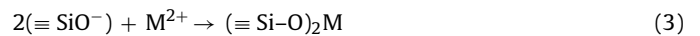
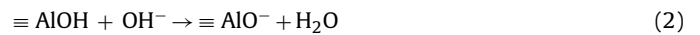
3.9. Adsorption mechanism

On the surface of the fly ash the functional oxidized groups are present as SiO_2 and Al_2O_3 . The surface of silica (SiO_2) has a high affinity towards metal ions [12]. The central ion of silicates (Si^{4+}) has a very strong affinity for electrons; therefore, the oxygen atoms that are bound to the silicon ions have a low basicity, making the silica surface act as a weak acid. The oxygen atoms on the silica surface are free to react with water, forming surface silanol (SiOH) groups. The acidity of the silanol (SiOH) groups determines the dependence of the charge of the silica surface on pH. At low pH, a positively charged silica surface results, and at high pH values negatively charged surface prevails. Alumina and iron also show the same phenomenon of developing positive or negative charges depending on pH.

In this study, the adsorption experiments were carried out in the alkaline pH (around 8.1). From the point of zero charge of the fly ash (pH_{ZPC} 6.9), it was found that the silica, alumina and iron content of the fly ash were negatively charged above 6.9 pH value. The negative charge at an active site on the surface of the fly ash

**Fig. 14.** FTIR spectrum of fly ash before and after adsorption.

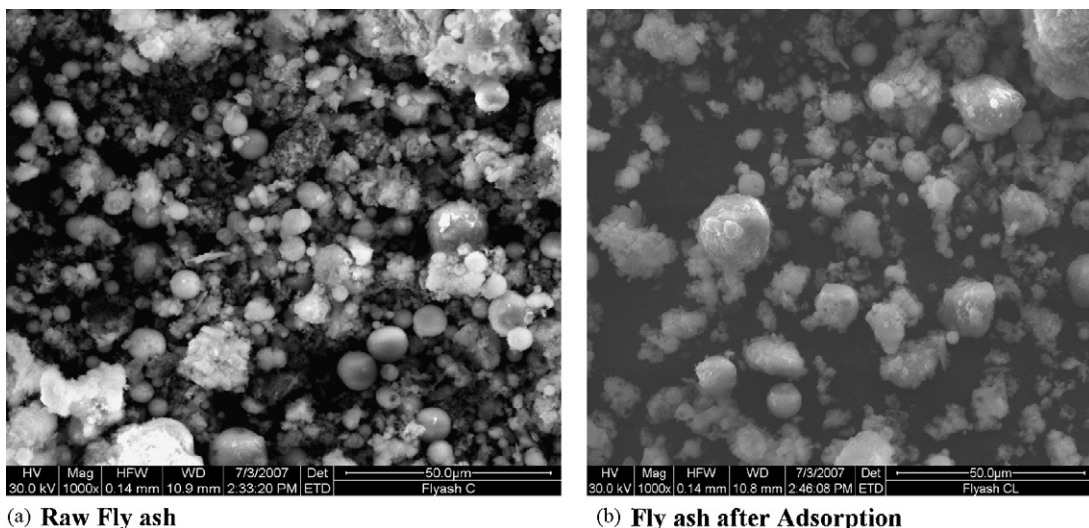
(Eq. (1) and (2)) which allows metals (M^{2+}) and metal hydroxides ($M(OH)_2$) to be complexed at the surface (Eq. (3)–(5)) [46,47].



where \underline{SO}^- are the free surface sites on fly ash.

3.10. Characterization of adsorbent after adsorption

In order to understand the morphology of adsorbent on the fly ash, both SEM and FTIR analyses of fly ash samples after adsorption were carried out and are shown in Fig. 13 and Fig. 14 respectively. The comparison of SEM picture (Fig. 13) between the raw fly ash and the fly ash after adsorption shows that there are morphologi-

**Fig. 13.** Morphology of fly ash before and after adsorption.

cal changes in the fly ash samples after adsorption. It was observed that the spherical balls of the fly ash particles are covered by precipitates and complexes formed by the heavy metal ions. Fig. 14 shows the comparison of observed FTIR peaks of fly ash before and after adsorption. The intensity of broad band at 3424 cm^{-1} is moved downward after adsorption. This is due to the solubility calcium content and ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) content of fly ash in the leachate during adsorption process and used to increase the leachate pH. This in turn decreases the percentage transmittance of hydroxyl groups present in the fly ash after adsorption. The percentage transmittance of peaks corresponding to $516, 779, 799$ and 1099 cm^{-1} are increased in the fly ash after adsorption. The active sites such as silica and alumina present on the fly ash samples were declined after adsorption as indicated by increasing of the percentage transmittance [33]. This confirms that adsorption of heavy metals has taken place on the active sites of fly ash such as silica and alumina according to the Eq. (3)–(5).

4. Conclusions

The present study has demonstrated that fly ash possesses the adsorption capacity for removal of heavy metal ions and organic compounds in leachate. The following are the conclusions arrived from this study.

The optimum dose of fly ash for heavy metal removal is found to be 2 g/L with the removal efficiencies of 39%, 28%, 74%, 42% and 71% for Cu, Mn, Pb, Zn and Cd respectively. However, low removal efficiencies of 5.5% and 28% were observed for TDS and COD respectively for the same optimum fly ash dose. Thus, it can be concluded that the fly ash is very effective as an adsorbent for lead and cadmium compared to other heavy metals.

The use of fly ash in leachate treatment is recommended in order to remove the heavy metals before discharging the treated leachate into near by water courses.

The uptake behaviour of fly ash for heavy metal cations follows an order of $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+}$, and the Freundlich isotherm was fitting well for the adsorption of heavy metals on the fly ash.

It is found that the adsorption kinetics of the metal ions (Cu, Pb and Cd) on fly ash follow the pseudo second-order type kinetic reaction and thus the adsorption rate-limiting step could be inferred as chemical sorption or chemisorption. On the other hand, for the Mn and Zn metal ions, the intraparticle diffusion model was found to be a best-fit model with 'α' values being higher than 0.50, confirming that the rate limiting step for these metals is intraparticle diffusion.

The fly ash after the utilization for the adsorption of heavy metals can be effectively disposed in the secured landfill along with hazardous waste.

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