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TREATMENT OF ASH LEACHATE USING DIFFERENT FUNCTIONAL GROUP ANION EXCHANGE RESINS

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Abstract

Fly ash leachate wastewater containing a wide variety of toxic heavy metals either in cationic or oxyanionic forms. Treatment of such water represents a challenge for all researchers due to the higher concentrations and competitive effect of all the existing cations and anions. The process of treatment was investigated using different functional groups anion exchangers to reach the most suitable materials and conditions for lowering the level of contamination for the wastewater reuse. The effects of most abundant anionic species in leachate wastewater such as sulfate on the adsorption of boron, molybdate, chromate, arsenate and selenate oxyanions were studied at different experimental conditions. The data obtained indicate that LAYNAE^{RT} is the most suitable anion exchanger for the removal of arsenate and selenate, whereas, IRA743 and A400 are good for the removal of boron and molybdate respectively.

Keywords: Leachate water treatment, ion exchangers and oxyanions.

Introduction

Fly ash is one of the residues generated in [combustion](#), and comprises the fine particles that rise with the flue gases. Ash which does not rise is termed [bottom ash](#). In an industrial context, fly ash usually refers to ash produced during combustion of [coal](#). Fly ash is generally captured from the chimneys of [coal-fired power plants](#), and together with [bottom ash](#) removed from the bottom of the furnace is in this case jointly known as coal ash. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of [silicon dioxide](#) (SiO₂) (both [amorphous](#) and [crystalline](#)) and [calcium oxide](#) (CaO), both being endemic ingredients in many coal-bearing [rock strata](#).

Toxic constituents depend upon the specific [coal bed makeup](#), but may include one or more of the following elements or substances in quantities from trace amounts to several percents: [arsenic](#), [beryllium](#), [boron](#), [cadmium](#), [chromium](#),

[chromium VI](#), [cobalt](#), [lead](#), [manganese](#), [mercury](#), [molybdenum](#), [selenium](#), [strontium](#), [thallium](#), and [vanadium](#), along with [dioxins](#) and [PAH compounds](#). [1][2]

In the past, fly ash was generally released into the [atmosphere](#), but [pollution control equipment](#) mandated in recent decades now require that it be captured prior to release. In the [USA](#), fly ash is generally stored at coal power plants or placed in landfills. About 43 percent is recycled, [3-10] often used to supplement [Portland cement](#) in concrete production. Some have expressed health concerns about this [11-15].

Fly ash material solidifies while suspended in the exhaust gases and is collected by [electrostatic precipitators](#) or filter bags. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally [spherical](#) in shape and ranged in size from 0.5 to 100 μm . They consist mostly of [silicon dioxide](#) (SiO_2), which is present in two forms: amorphous, which is rounded and smooth, and crystalline, which is sharp, pointed and hazardous; [aluminum oxide](#) (Al_2O_3) and [iron oxide](#) (Fe_2O_3). Fly ashes are generally highly [heterogeneous](#), consisting of a mixture of glassy particles with various identifiable crystalline phases such as [quartz](#), [mullite](#), and various [iron oxides](#).

Two classes of fly ash are defined by [ASTM C618](#): Class F fly ash and Class C fly ash. The chief difference between these classes is the amount of calcium, silica, alumina, and iron content in the ash. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e., [anthracite](#), [bituminous](#), and [lignite](#)) [14-20].

Not all fly ashes meet ASTM C618 requirements, although depending on the application, this may not be necessary. Ash used as a cement replacement must meet strict construction standards, but no standard environmental regulations have been established in the United States. 75% of the ash must have a [fineness](#) of 45 μm or less, and have a [carbon](#) content, measured by the loss on ignition (LOI), of less than 4%. In the USA, LOI needs to be fewer than 6%. The particle size distribution of raw fly ash is very often fluctuating constantly, due to changing performance of the coal mills and the boiler performance. This makes it necessary that fly ash used in concrete needs to be processed using separation equipment like mechanical air classifiers. Especially important is the ongoing quality verification. This is mainly expressed by quality control seals like the [Bureau of Indian Standards](#) mark or the DCL mark of the Dubai Municipality.

This study investigated the adsorption of Se, Cr and Mo oxyanions using five different anion exchanger namely LAYN^{RT}, HAIX, A400P, IRA900 and IRA743 as

a model for strong anion exchangers (quaternary ammonium functional group) whereas IRA743 as a model for weak base anion exchanger (tertiary amine functional group). Structure characteristics of these anion exchangers were illustrated in Table 1.

Table 1: Structure characteristics of the anion exchangers

Resin	A400	HAIX	LAYNE ^{RT}	IRA 900	IRA743
Type	Strong Base				
Matrix	Macroporous	Gel	Macroporous		Gel
Capacity (eq/l)	Polystyrene Cross-linked with Divinylbenzene				
	1.3	1.9		1	0.6
Functional group	Quaternary ammonium	Quaternary ammonium Hydrous iron oxide +		Quaternary ammonium	N-Methylglucamine

The aim of this work is to investigate the treatment of leachate wastewater using different functional groups anion exchanger (LAYN^{RT}, HAIX, A400, IRA900 and IRA743). The effect of competing SO₄²⁻ anions was also investigated at different concentration (120 – 10,000 ppm).

Fly ash also contains environmental toxins in significant amounts, including [arsenic](#) (43.4 ppm); [barium](#) (806 ppm); [beryllium](#) (5 ppm); [boron](#) (311 ppm); [cadmium](#) (3.4 ppm); [chromium](#) (136 ppm); [chromium VI](#) (90 ppm); [cobalt](#) (35.9 ppm); [copper](#) (112 ppm); [fluorine](#) (29 ppm); [lead](#) (56 ppm); [manganese](#) (250 ppm); [nickel](#) (77.6 ppm); [selenium](#) (7.7 ppm); [strontium](#) (775 ppm); [thallium](#) (9 ppm); [vanadium](#) (252 ppm); and [zinc](#) (178 ppm) [5].

Experimental

2.1 Materials

All anion exchangers are purchased in sodium form

Fly ash leachate samples were handled and supplied by Electric Power Research Institute The Electric Power Research Institute (EPRI)

Treatment using Batch test

200 ml of the analyzed samples were shaken for 24 hours with appropriate amount of adsorbent to reach equilibrium

Instrumentation

Determination of oxyanions

Determination of Mo was performed using a UV/VIS spectrometer (Perkin–Elmer, Lambda 2). Total dissolved As and Se and Cr analyses of samples were carried out using a Perkin Elmer atomic absorption spectrophotometer (AAS) with graphite furnace accessories (Model SIMAA 6000) and an electrodeless discharge lamp (EDL).

Results and Discussion

Characterization of fly ash

Elemental analysis

Fly ash also contains environmental toxins in significant amounts, including [arsenic](#) (43.4 ppm); [barium](#) (806 ppm); [beryllium](#) (5 ppm); [boron](#) (311 ppm); [cadmium](#) (3.4 ppm); [chromium](#) (136 ppm); [chromium VI](#) (90 ppm); [cobalt](#) (35.9 ppm); [copper](#) (112 ppm); [fluorine](#) (29 ppm); [lead](#) (56 ppm); [manganese](#) (250 ppm); [nickel](#) (77.6 ppm); [selenium](#) (7.7 ppm); [strontium](#) (775 ppm); [thallium](#) (9 ppm); [vanadium](#) (252 ppm); and [zinc](#) (178 ppm)[5].

Scanning Electron Microscope (SEM)

The SEM image of fly ash indicates the spherical shape of the particles Fig. 1

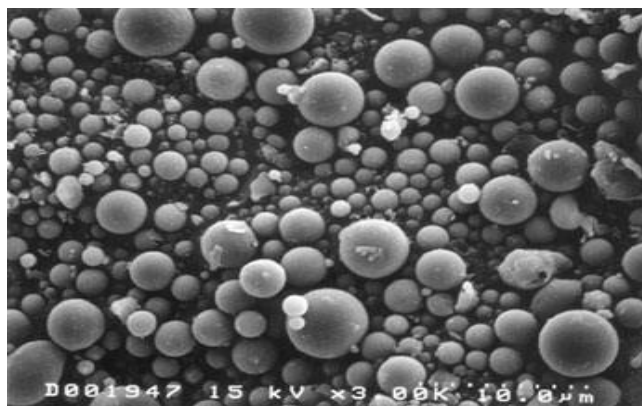


Fig. 1. Photomicrograph made with a Scanning Electron Microscope (SEM): Fly ash particles at 2,000 x magnification [6]

Fly ash leachate treatment

Effect of resin type

Investigation of the effect of functional group on the treatment of leachate wastewater samples have been studied at lower sulfate concentration (120 ppm) and represented in Table 2. The data obtained indicate that in case of using HAIX and LAYNE^{RT} resins a complete removal of As have been observed since these resins were modified with FeOOH functional group which have the ability and selectivity for As removal. Furthermore, the using of A400 and IRA 900 indicate a lower removal of As when compared with HAIX and LAYNE^{RT}. On the other hand the use of IRA 743 shows no As removal due to the nature of the functional group of this resin which is selective for the removal of boron.

Table 2. Treatment of synthetic leachate

Feed Composition

- As = 544 µg/l
- Mo = 4 mg/l
- Cr = 3.7 mg/l
- Se = 1.689 mg/l
- B = 5.0 mg/l
- SO₄²⁻ = 2000 ppm
- pH = 7.5

Type of Resin Elements	LAYNE ^{RT}		HAIX		A400		IRA900		IRA743	
	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1
As (µg/l)	0.5	0.1	0.5	0.1	53	50	51	488	54	54
	ND	ND	ND	ND	2	5	8		4	4
Cr (mg/l)	0.9	0.4	1.5	1.1	2.0	1.5	ND	ND	3.7	3.6
		3		6		8			2	4
Mo (mg/l)	3.5	3.8	4.3	4.3	4.2	4.2	4.3	4.3	3.7	3.8
					3	8	5		5	2
Se (mg/l)	1.1	0.9	1.3	1.0	1.3	0.9	1.2	0.87	1.6	1.6
		4				5			9	9
B (mg/l)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	ND	ND

The data depicted for chromate removal were represented in Table 2. The data indicate that IRA 900 exhibits a very good removal for chromate, whereas the use of LAYNERT, HAIX, A400 exhibit a moderate removal of chromate if compared with IRA 900. On the other hand, IRA743 does not indicate any chromate removal at the

working pH (7.5) due to the inactivity of weak base anion exchanger at the neutral pH.

Investigation of Se anions removal is represented in Table 3. It is clear that a good removal efficiency of Se was observed upon using of LAYNE^{RT}, HAIX and A400 resins, whereas using of IRA 900 showed lower removal efficiency.

Effect of SO₄²⁻ anions

Anionic adsorbates directly compete for available binding sites and indirectly interact through alternation of the electrostatic charge at the resin surface. The effect of sulfate (2000, 5000 and 10000 ppm) as the most highly concentrated anion in leachate water samples has extensively investigated due to its great competition with the other anions and oxyanions.

Table 3. Effect of SO₄²⁻ on the removal of As (544 µg/l)

SO ₄ ²⁻ Conc. (mg/l)	Equilibrium As Conc. (µg/l)									
	LAYNE ^{RT}		HAIX		A400		IRA 900		IRA743	
	0.5	1	0.5	0.1	0.5	1	0.5	1	0.5	1
120	ND	ND	ND	ND	478	412	332	189	544	544
2000	ND	ND	ND	ND	ND	ND	391	276	544	544
5000	ND	ND	ND	ND	195	121	413	325	544	544
10000	ND	ND	ND	ND	439	327	498	415	544	544

The data recorded for sulfate effect on the removal of As are depicted in Table 3. It's clear that the adsorption of As is not influenced by changing sulfate concentration upon using HAIX and LAYNE^{RT} resins. Sengupta [21] explored the phenomena of As forming an inner-sphere complex and sulfate forming an outer-sphere complex on HFO sites. Since the inner-sphere anion is a stronger adsorbate than the outer-sphere anion. However, upon using A400 and IRA 900 anion exchangers the increasing of sulfate concentration strongly influence the removal of As.

The data obtained for the removal of the above mentioned oxyanions are depicted in Table 4, 5&6. The results show that increasing of sulfate concentration more than 120 mg/l completely suppress the adsorption of chromate, selenate and molybdate oxyanions.

Table 7 summarizes the net results obtained from this study.

Table 4. Effect of SO₄²⁻ on the removal of Cr (5 mg/l)

SO ₄ ²⁻ Conc. (mg/l)	Equilibrium Cr Conc. (mg/l)									
	LAYNE ^{RT}		HAIX		A400		IRA 900		IRA743	
	0.5	1	0.5	0.1	0.5	1	0.5	1	0.5	1
120	ND	ND	ND	ND	0.76	0.3	ND	ND	3.7	3.7
2000	0.9	0.42	1.49	1.16	2.030	1.58	ND	ND	3.72	3.64
10000	3.45	2.52	3.57	3.02	3.59	3.22	1.38	0.22	3.7	3.7

Table 5. Effect of SO₄²⁻ on the removal of SeVI (1.73 mg/l)

SO ₄ ²⁻ Conc. (mg/l)	Equilibrium Se VI Conc. (mg/l)									
	LAYNE ^{RT}		HAIX		A400		IRA 900		IRA743	
	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1	0.5	1
120	0.1	0.1	0.36	0.23	0.8	-	1.2	0.87	1.8	1.8
2000	1.1	0.94	1.3	1.06	1.3	1.13	1.6	1.04	1.8	1.8
5000	1.5	1.4	1.67	1.22	1.4	1.25	1.8	1.8	1.8	1.8
10000	1.7	1.63	1.79	1.82	1.65	1.58	1.8	1.8	1.8	1.8

Table 6. Effect of SO₄²⁻ on the removal of Mo (4 mg/l)

SO ₄ ²⁻ Conc. (mg/l)	Equilibrium Mo Conc. (mg/l)									
	LAYNE ^{RT}		HAIX		A400		IRA900		IRA743	
	0.5	1	0.5	1	0.5	1	0.5	1	0.5	1
120	3.5	3.2	3.7	3.3	2.2	1.3	1.12	ND	4	4
2000	4	4	4	4	4	4	4	4	4	4
5000	4	4	4	4	4	4	4	4	4	4
10000	4	4	4	4	4	4	4	4	4	4

Table 7. Summary of the obtained results

Resin	A500P	A400	HAIX	LAYNE ^{RT}	IRA 900	IRA743
As Removal efficiency	Poor		Excellent at any sulfate concentration		Poor	Poor
Se Removal efficiency	Very good at lower sulfate concentration		Very good at lower sulfate concentration		Moderate at lower sulfate concentration	Poor
Cr Removal efficiency	Very good at lower sulfate concentration		Very good at lower sulfate concentration		Excellent at any sulfate concentration	Good at lower pH
B Removal efficiency	Poor		Poor		Poor	Very good
Mo Removal efficiency	good at lower sulfate concentration		Poor		Poor	Poor
Removal mechanism	Ion exchange process					

Conclusion

The treatment of leachate water was carried out using different functional groups ion exchange resins. The data obtained indicated the great influence of sulphate species on the removal of toxic oxyanions except arsenic which show a high removal capacity even with high sulphate concentration.

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