

FLY ASH AS A ADSORBENT FOR REMOVAL OF HEAVY METAL: A REVIEW

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Abstract: Adsorption is a fundamental process in the physicochemical treatment of wastewaters. The coal fly ash is a waste material that generate from industrial processes. It is a cheap, eco-friendly and bio degradable material. Long term exposure of human bodies to heavy metals susceptible to receives various infection and diseases from an environmental and economic perspective. Adsorption is acceptable process that can be applied in wastewater treatment, these waste materials pollute our environment or ecosystem and pose the problem of their disposal so “use waste to treat the water” is the concept to avoid the environment pollution. The application of available adsorption models such as the isotherm, kinetics and thermodynamics as well as the influence of parameter on metal adsorption by low cost adsorbent shall be reviewed to understand the adsorption mechanism of low-cost adsorbent. In this review study the chemical composition of different coal fly ash and fly ash for the removal of heavy metal ions are summarized.

Keywords: Fly ash, Heavy metals, Adsorption, Environment, Wastewater.

Introduction

Quality of water and management of waste is most important proposition in human life. Accretion of technologies in industrialization and urbanization lead to increase in percentage accumulation of waste all around the globe and release of heavy metal in the water streams from different activities such as industrial, agricultural and domestic¹.

Water is a basic source of life and thus is essential element to all living things on earth. Technological development and industrial activities cause heavy metal pollution is posing significant threats to the public health and environment because of its toxicity, non-biodegradability, bioaccumulation and persistent tendency through food chain².

Process of adsorption is operate in chemical, biological and physical system for the use of removing substances from any liquid or gaseous solution. Adsorption process involve separation of a substance from one phase accompanied by its concentration at the surface of another involves adsorption. Adsorption efficiency depends on activated carbon, temperature, pH and adsorbate. Heavy metals from industrial wastewater can be removed by adsorbent³. Heavy metals are toxic in nature therefore it is essential to remove from wastewater. Adsorption is very common method for removal of heavy metals from wastewater. So many researchers used fly ash as adsorbent for removal of organic material and heavy metals from wastewater⁴.

The aim and objective of this review paper is to provide fundamental information and literature in fly ash as a adsorbent for removal of heavy metals.

Composition of fly ash

Fly ash particles are generally spherical in shape and range in size from 0.5 μ m to 100 μ m⁵. Fly ash material solidifies while suspended in the exhaust gases and is collected by electrostatic precipitators or filter bags. Table 1 showed the chemical composition of coal fly ashes.

Table-1: Chemical composition of coal fly ashes

Source of coal fly ash	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	MgO	SO ₃	CaO	K ₂ O	Na ₂ O	LOI	P ₂ O ₅	Other	Reference
Thermal power, India	38-63	27-44	0.5-1.8	3.3-6.4	0-0.5	0.01-0.5	-	0.2-8	0.04-0.9	0.07-0.43	0.2-3.4	-	-	6
Brasov CHP Plant (CET), Romania	53.32	22.05	1.07	8.97	0.08	2.44	1.4	5.24	2.66	0.63	1.58	0.12	-	7
Thermal power, Kosova	26.75	4	0.50	10.77	-	4.36	-	41.48	0.16	1.42	2.20	-	-	8
Geos Company, Egypt	89.56	4.74	-	4.24	-	0.13	-	0.01	-	-	0.8	-	0.52	9
Thermal power, Macedonia	46.83	25.9	0.62	8.96	0.19	2.99	-	6.86	2.56	1.50	-	0.34	-	10
Electricity Generation Company, Tuncbilek, Turkey	61.5	22.0	0.72	8.00	-	3.70	0.84	1.90	1.40	-	-	-	-	11
Unchahar Thermal Power Station, Singrauli, MP, India	61.10	25.02	-	6.92	-	0.53	-	1.69	-	-	2.6	-	4.94	12
Thermal power, India	62	26	1.8	6.3	-	0.49	-	1.13	1.28	0.28	-	0.40	SO ₄ -0.36	13
Thermal Power Plant Koradi, Nagpur, MH, India	62.6	24.41	0.69	4.04	0.28	0.54	0.84	0.35	0.21	0.27	1.27	0.03	-	14
South Africa	37.81	24.67	1.8	4.84	-	0.22	-	1.19	0.74	0.11	-	-	B ₂ O ₅ -0.05, Cr ₂ O ₃ -0.03, Bao-0.14	15
Koradi Thermal Power Plant, Nagpur, MH, India	40.45	16.75	-	4.13	-	2.58	-	3.67	-	-	-	-	-	16
Koradi Thermal Power Plant, Nagpur, MH, India	65.01	24.41	0.69	4.04	0.28	0.55	0.15	0.35	0.21	0.22	2.04	0.03	-	17
Muja Power Station, Collie, Australia	55	29	-	8.8	-	1.0	-	1.6	-	-	-	-	-	18
Alborz-e-Sharghi Coal Company, Shah Road, Iran	37.88	28.73	-	18.07	-	1.79	0.38	11.54	0.34	0.29	-	-	-	19
Thermal power, Egypt	68.01	1.34	0.07	0.25	-	2.39	-	5.77	2.09	0.76	17.25	0.39	SO ₅ -1.44	20
Rzeszow-Zaleze Electric Power Station, Poland	50.3	32.6	-	5.13	-	1.46	-	1.30	2.79	0.56	-	-	-	21
Thermal Power Plant Kozienice, Poland	48.78	22.2	1.24	8.71	0.08	1.96	1.02	4.10	3.31	2.96	-	0.86	ZnO-0.05, Cr ₂ O ₃ -0.03, NiO-0.02, CuO-0.02, Bao-0.07	22
Can Thermal Power Plant, NW, Turkey	32.24	20.73	0.67	5.57	0.11	0.55	-	21.51	0.33	0.97	5.10	1.21	Cr ₂ O ₃ -0.005	23

Steren Janakuasa Electric Sultan Abdul Aziz Shan, Kapar, Selangor, Malaysia	59.00	21.00	-	3.70	-	1.40	1.00	6.90	0.90	-	4.62	-	-	24
Catalagzi, Turkey	57.5	29.2	1.03	4.85	-	2.2	0.28	0.95	3.44	0.5	-	-	-	25
Neyvelli, Tamil nadu, India	50.97	18.81	0.28	16.61	-	1.41	-	9.00	0.23	0.18	2.60	-	-	26
Thermal Power Plant, Iran	20-60	5.0-35	-	10.0-40	-	-	-	1.0-12	-	-	0-15	-	-	3
Thermal Power Plant, Egypt	57.82	22.10	-	8.33	-	-	-	-	-	-	-	-	-	27
Thermal Power-Plant, Koradi, Nagpur, MH, India	65.01	24.41	0.69	4.04	0.28	0.55	0.15	0.35	0.21	0.22	2.04	0.03	-	28
Cayirhan, Turkey	50.30	11.20	0.50	8.05	-	4.90	5.25	14.50	1.60	3.30	-	0.40	-	29
Vijayawada(VTPS) AP, India	63.14	24.50	-	3.00	-	1.65	2.25	2.15	-	-	1.20	-	-	30
CPH Plant CET Bresov, Romania	53.32	22.05	1.07	8.97	0.08	2.44	-	5.24	2.66	0.63	1.58	-	-	31
Dirk India PVT.LTD, Nashik, India	89.56	4.74	-	4.24	-	0.13	-	0.01	-	-	0.8	-	0.52	32
Tanjung jati B Thermal power Plant, Indonesia	36.47	19.27	-	10.74	0.07	2.94	1.04	6.56	1.77	1.76	-	0.25	CuO-0.01, AS ₂ O ₃ -0.01, C-19.11	33
Thermal power Plant, Chachai, Anoopur, Shahadol, India	59.54	27.20	-	4.87	-	0.40	-	2.91	-	1.00	12.00	-	-	34
Thermal power Plant, India	62.6	24.41	0.69	4.04	0.28	0.54	0.84	0.35	0.21	0.27	1.27	0.03	-	35
Shenhua Guohua Jinjie Power Station, China	33-54	18-56	-	2.0-7	-	0.3-1.7	0.8-1.8	1.0-13	0.4-3.8	0-1.1	-	-	-	36
Thermal power Plant, Bokaro, Jharkhand, India	60.25	28.79	2.41	5.5	-	0.27	0.21	0.64	0.97	0.32	-	0.66	-	37
Thermal power Plant, Tuticorin, Tamil Nadu, India	66.07	21.15	-	4.90	-	0.81	-	4.41	-	-	0.41	-	-	38
Iasi Thermal power Plant, Romania	37.41	8.31	1.40	2.52	-	0.78	-	7.69	0.72	-	-	0.46	C- 14.87, N- 5.26, O- 20.58	39
Catalagzi, Zongwdak, Turkey	57.2	25.1	-	7.3	-	1.8	0.2	1.7	4.8	0.4	1.6	-	-	40
Delmarva Power Plant, Wilmington New Yark, USA	43.6	31.4	-	8.2	-	-	-	6.9	4.5	-	-	-	-	41
Thermal power, United States, America	45-65	20-45	-	3.0-12	-	1.0-3	1.0-5	3.0-10	-	-	0.1-6	-	-	42
WSRA Shaanxi Provinc- China	52.2	29.3	1.01	3.83	0.051	0.73	-	4.90	1.87	0.50	-	-	5.58	43
Thermal power, BQRA China	51.5	30.9	1.10	4.88	0.065	0.61	-	7.18	1.25	0.56	-	-	1.86	-, -
NTPC - Dadri, Dist Gautambudh Nagar, UP, India	51.98	28.55	-	4.91	-	1.54	1.47	8.67	1.80	0.24	2.31	-	Cl-0.0053, Free Lime	44

													0.64	
NLC Power Plant Neyveli, Tamil Nadu, India	1.86	24.87	2.54	1.14	-	5.53	-	10.9	-	-	-	-	-	45
Thermal power, Kutch, Gujrat, India	22.74	17.80	5.44	13.33	0.98	2.80	8.17	10.52	15.34 ppm	173 ppm	-	0.04	K ₂ O ₃ - 37.60	46
Thermal power, Taiwan	52.5	27.9	-	6.3	-	1.6	0.79	6.27	-	-	5.01	-	-	47
Male Moh Electric Power Plant, Thailand	38.12	23.08	-	8.72	-	2.09	-	13.92	-	-	-	-	-	48
Power Plant Soma, Turkey	33.41	16.13	-	6.00	-	6.07	2.80	33.77	0.66	1.04	-	-	Bao-0.15	49
Thermal power, Yatagan, Turkey	36.43	16.13	-	7.77	-	8.80	6.83	23.51	0.77	1.05	-	-	Bao-0.15	-,-
Rutenberg Power Plant Yenikoy, Turkey	20.79	17.26	-	7.17	-	4.66	12.80	38.24	1.33	2.19	-	-	Bao - 0.13	-,-
South African	40.9	31.4	24	3.05	-	2.45	0.35	8.35	-	0.02	-	-	-	-,-
Thermal power, Rajasthan, India	55.19	30.12	2.96	4.62	-	1.93	-	0.76	1.40	2.21	-	-	Bao-1.30	50
Thermal power, Rajasthan, India	58.32	28.69	3.20	4.42	-	2.10	-	0.60	0.80	1.88	-	-	Bao-0.23	-,-
Bakreswar Thermal power plant, West Bengal, India	62	26	1.8	63		0.49		1.13	1.28		0.40		So ₄ -0.36	51
H.E.G. Thermal power plant, Mandideep, MP, India	55.26	22.75	2.95	7.12		0.63	1.58	4.10	2.14	1.23	4.10	1.65		52
Thermal power plant, Harbin No.3, China	55.7	25.9	0.7	3.3		0.3		3.7	2.4	0.2	5.4			53
Thermal power plant, Bryung, Chungnam, Korea	50.0	28.7		3.7				2.6		0.3	0.3		5.6	54

Toxicity and sources of Heavy metals in waste water

On the basis of health significance heavy metals are classified in to four major groups- Essential: Cu, CO, Cr, Fe, Mn, Zn. Non-essential: Al, Ba, Li, Zr. Low toxic: Al, Sn. High toxic: Cd, Hg. Heavy metals due to toxic effects in plants, human and food are kept under environmental pollutant category. Heavy metals like Arsenic (As), Cadmium (Cd), Lead (Pb), Mercury (Hg) are cumulative poison. This heavy metals are persistence, accumulate and not metabolized in other intermediate compounds and do not easily break in the environment. These metals are accumulating in food chain through at primary producer level and then through consumption at consumer level. Heavy metals like Cd, Ni, As, Pb are harmful to humans. These metals are potent carcinogenic and mutagenic³.

Table- 2: Effects of heavy metals

Heavy Metals	Effects	References
Ni	Chronic asthma, coughing, human carcinogen, leucopenia and lymphopenia, skin dermatitis, nausea,	53-54
As	Vascular disease, visceral cancers, skin manifestations	55
Pb	Diseases of the kidneys, circulatory system and nervous system, damage the fetal brain	-, -
Hg	Rheumatoid arthritis, diseases of the kidneys, circulatory system and nervous system	-, -
Cd	Renal disorder, human carcinogen, kidney damage, high blood pressure, destruction of testicular tissue and red blood cells	56
Zn	Lethargy, depression, neurological signs and increased thirst, stomach cramps, skin irritation vomiting and respiratory disorders	-, -
Ba	vomiting, abdominal cramps, diarrhea, difficulties in breathing, increased or decreased blood pressure, numbness around the face and muscle weakness, changes in heart rhythm or paralysis and possibly death	57
Cr	Nausea, lung cancer, skin uncertainty, skin irritation and corrosion of skin, ulcer formation, liver damage, respiratory tract infection, severe diarrhea, epigastric pain, hemorrhage	58
Cu	Cancer, heart disease, anorexia, anemia and anxiety, Wilson disease, insomnia, liver damage	59
Mn	Change of hair colour, fatness, birth defects, neurological symptoms, glucose intolerance, skin problems, blood clotting, lowered cholesterol levels, skeleton disorders	60

Source of heavy metals that penetrate in to the water system can derive from both natural and anthropogenic sources. The main source of heavy metal contamination exists in aqueous wastes of many industries, such as mining, operations, chloralkali, smelting, tanneries, metal plating, alloy industries, radiator manufacturing and storage batteries industries.

Conventional process for heavy metal removal

Numerous treatments on the heavy metal removal from contaminated water have already been applied years ago which can be divided in to physical, chemical and biological processes. However, in most treatments, physical and chemical process is more pronounced. The conventional method for heavy metal removal includes metal precipitation, ultra filtration, biological systems, oxidation, solvent extraction, electrolytic processes, ion exchange, membrane filtration and adsorption. Physical and chemical treatment is more costly compared to biological treatment in removing metal however biological treatment are low effectiveness and longer process⁶¹.

Adsorption

Adsorption is the surface phenomenon in which accumulation of atoms or molecules take place on the surface of a material. Adsorption has two components adsorbent and adsorbate. Adsorbent is a substance on which adsorption takes place. Adsorbate is the substance which gets adsorbed on surface. In general adsorption is a removal process where certain particles are bound to an adsorbent particle surface by either physical or chemical attraction. The process of adsorption arises due to presence of residual or unbalanced forces that arise on the surface of material and these residual forces have tendency to attract and retain the species or atoms with which it comes in contact with a surface. The reverse of this process is called desorption⁶².

Adsorption can be categorized in to two types:

1. Physical adsorption

It is a general incident and occurs in any liquid/solid or gas/solid system. In which binding of adsorbate on the adsorbent surface is caused by Vander Waals forces of attraction. The electronic structure of the atom or molecule is hardly disturbed upon physical adsorption.

2. Chemical adsorption

It is a kind of adsorption which involves a chemical reaction between the adsorbent and the adsorbate. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds (covalent, ionic). The adsorbate can form a monolayer. It is utilized in catalytic operations⁵¹.

Factors affecting the adsorption of heavy metals

Various factors influence the adsorption capacity of potential adsorbents during the adsorption process.

Effect of pH: pH is determination of adsorption in terms of hydrogen ion concentration. On increasing pH of the sorption system, the adsorptive capacity of metal cations increases but not in linear relationship. Sorption not occurs at highly acidic and alkaline conditions because hydrogen ions and hydroxyl ions compete for active sites on adsorbents surface².

Effect of Adsorbent dosage: Dose of adsorbent also is one of the main points to determine the capacity uptake of heavy metals. Generally, increase in the dose of adsorbents will increase in the adsorbed capacity until its reach a limit. If further increase the dose, the adsorption capacity will be constant¹.

Effect of initial concentration: Initial concentration of metal ions can alter the metal removal efficiency through a combination of factors such as the availability of specific surface and the ability of surface functional groups to bind metal ions. Initial concentration of solution can provide an important driving force to overcome the mass transfer resistance of metal between the aqueous and solid phases⁵³.

Effect of contact time: More complete adsorption will be achieved if longer the contact time or retention but as the equilibrium has been achieved there is no increase in % removal of metal ion².

Effect of temperature: The nature of the process either endothermic or exothermic is depends on the adsorption equilibrium that affected by the temperature used. The uptake capacity of the adsorbents increases with the rises of the temperatures¹.

Table-3: Summary of fly ash for the removal of heavy metal ion

Heavy Metal	Optimized Conditions	% Removal or Uptake (MGLG)	E/K Model	References
Ni	pH - 0-14 Particle Size- 75µm Adsorbent Dose-3.5g/l Contact Time – 4-8h Temp. - 0-100°C	98 %		39
Ni	pH - 3-9, Adsorbent Dosage - 1-10 g/l IMC - 350-650 mg/l Contact Time - 300 min Temp. - 20-40°C	Maximum Monolayer Adsorption Capacity of CFA was found to be 294.00 mg/g	L and F, D-R Dublin-Radush-Kevich	40
Ni	pH-5.5-9.0 Particle Size below 75µm IMC - 20 mg/l Contact Time - 3 hours	90-95 %	Pf, Ps, L and F	28
Ni	pH - 6.9 to 7.9 Particle Size below 75µm IMC - 20mg/l Contact Time - 3 hours	91.12 %		17
Cd, Zn	pH -5- 6, Adsorbent Dosage - 10 gL ⁻¹ IMC - 10 mg L ⁻¹ Contact Time 120 min Temp. - 30-50°C	86.9 % Zn, 81.8 % Cd	Ps, Pf , L, F, Temkin,	54
Cd	pH - 2.0-12.0 Adsorbent Dosage-5.0-25.0 g/L IMC – 10.0-70.0 mg/l Contact Time - 0-360 min Temp. - 303k, 313k, 323k	80.27 %	L, F	12
Cd	pH - 2-12 Particle Size 75µm, IMC – 10- 100 mg L ⁻¹ Contact Time 5-7 h, Temp.- 25-45°C	84 %	Ps, L, F	19
Cd, Ni	Particle Size 1 to 30µm, Contact Time 10-60 min	Cd – 97 % Ni – 98 %	Ps L, F	4
Cr	pH - 8.0 Adsorbent Dosage 10g./25 ml Contact Time - 48 h	92 %	-	63
Cr	pH - 9.0 Adsorbent Dosage-2-16 g/L IMC – 50- 500 mg/l Contact Time 20 h Temp.- 150°C	76.4-83 %	Pf, Ps, L, F	64
Cr	pH – 3 Adsorbent Dosage-1.0 g IMC – 50 mg/l Contact Time 30 min	81.66 %	Pf, Ps , L, F	65

Cr	pH - 6.0 Adsorbent Dose 10 g L ⁻¹ IMC - 10 mg L ⁻¹ Temp. - 25°C	77.4% Untreated 85.4% Treated	Pf, Ps, L, F	30
Cu	pH - 4-6 Particle Size- 90µ, 300µ Contact Time - 60 min Temp. - 30°C	84.59%	F	66
Cu, Zn	pH - 8 Adsorbent Dosage- 0.2 gm to 2.5g Particle Size 50-150 µm Contact Time Cu - 60 min, Zn -55 min	Cu - 0.9932 Zn -0.9971	F	15
Cu, Zn	pH - 2-11 IMC - 50 mg/l Particle Size 28.7 µm Contact Time 2 h Temp. -105°C	Cu - 75.4 Zn - 56.8	Pf, Ps, L, F	21
Cu	pH - 4.5-5.0 IMC - 100mg/L Contact Time-2 h	75%	L, F	16
Fe	pH - 4 Contact Time-60 min Temp. -110°C Adsorbent Dosage- 2.5 gm	88.55%	L, F	66
Hg, Pb	Adsorbent Dosage- 15 gm /100 Particle Size -149-250 µm Contact Time- 200 min-350min Temp.-120°C	Hg-80% Pb-60%	Pf, Ps	67
Pb	Adsorbent Dosage-1.5 g/l Particle Size-52 µm Contact Time- 60 min IMC - 20- 140 mg/l Temp.- 300k	90.37 %	L, F	68
Pb	pH - 5.82 Particle Size-75 µm IMC -20mgL ⁻¹ Contact Time-3h	95.95 %	Pf, Ps, L, F	35
Zn	pH - 5.89 Particle Size-75 µm Contact Time- 1 h IMC - 10gm/100ml	100%	L, F	69
Zn	pH - 6-7.5 Particle Size- 75µm Temp. -0-55°C	95-99 %	L	41
Mn	pH - 8.0 Particle Size-100-250 µm IMC - 1.5-5.0mg Temp.-298k	74.2 %	-	70

Zn	pH – 1.0-6.0 IMC – 3.06×10^{-4} to 3.06×10^{-3} M Contact Time – 24 h Adsorbent Dosage – 5-20 g/l	100 %	-	71
Cu	pH – 3-10 Adsorbent Dosage-4g/l IMC – 80 mg/l Contact Time-60 h Temp. - 30°C	69.44 %	L	72
Zn	pH – 6 Adsorbent Dosage-4g/l Contact Time-1.15 h Temp.-303k	57.7 %	L	73
Cu	pH – 3.0-8.0 Particle Size-0.075 mm Adsorbent Dosage-10g/l IMC – 50-100 mg/l Contact Time-0-200 min Temp. -25°C, 45°C, 60°C	90 %	L, F	74
Zn	pH - 2-10 Particle Size- <300 µm Adsorbent Dose-0.2-1 g/l IMC – 25-200 ppm Contact Time – 5-60 min Temp. – 28±5°C	76.24%	L, F	75
As	pH - 5-12 Particle Size- 105.5 µm Adsorbent Dose-0.25-2.5 g/l IMC – 500 mg/l Contact Time – 24 h Temp. – 25°C	95 %	L, F	76
Cr	pH – 1-3 Adsorbent Dose-10 g/l IMC – 100-400 mg/l Contact Time – 6 h Temp. – 30°C	95 %	L, F	77

Adsorption Isotherm: An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase. Since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents and so are critical for design purposes; therefore, the correlation of equilibrium data using an equation is essential for practical adsorption operation⁹. Two isotherm equations were adopted in this study, as follows:

Langmuir isotherm equation: Based on Langmuir adsorption theory, molecules are adsorbed at a fixed number of well-defined active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between the adsorbed molecules⁵³.

The Langmuir isotherm is defined as

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e}$$

Where: q_e is equilibrium metal sorption capacity, c_e is equilibrium solute concentration in solution, q_{\max} and b are Langmuir constants related to maximum sorption capacity (monolayer capacity) and bonding energy of adsorption¹.

Freundlich isotherm equation: Freundlich isotherm model interprets the adsorption on heterogeneous surfaces with interactions occurring between the adsorbed molecules and is not restricted to the formation of a monolayer. This isotherm is commonly used to describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents⁷⁸.

The Freundlich isotherm is defined as

$$q_e = K_f C_e^{1/n}$$

Where: K_f is biosorption equilibrium constant, q_e is the sorption capacity, and n is a constant indicative of biosorption intensity.

Table-4 : Langmuir and Freundlich adsorption parameters for metal ion

Metal	Langmuir isotherm			Freundlich isotherm			References
	Qm(mg/g)	b	R ²	K _f (mg/g)	n	R ²	
Cr	0.595	0.028	0.994	0.034	0.034	0.992	59
Cr	7.057	0.6512	0.9376	1.740	2.150	0.9745	62
Cr	55.24	0.0405	0.994	3.11	1.562	0.9815	61
Pb	5.5248	0.1865	0.986	1.6536	3.4013	0.992	35
Zn	0.4488	0.1246	0.994	0.1641	5.0761	0.982	67
Cu	0.1825	21.124	0.9899	3.629	3.94	0.9243	9
Zn	0.1806	7.0	0.9783	1.139	15.848	0.8982	---
Cd	6.0277	6835	9608	0.2344	1.6226	0.9336	12
Cu	0.041	0.117	0.946	1.009	1.039	0.959	79
Ni	3.2499	14.2454	0.9818	13.0828	4.1169	0.9595	80
Zn	15.06	0.3076	0.9957	24.67	0.1	0.9174	81
Ar	5.8	0.1813	0.99	1.656	3.58	0.9042	82
Cd	7.502	0.017	0.999	0.00006	2.06	0.972	83
Cu	7.236	0.015	0.917	0,002	5.201	0.903	---
Cr	3.13	0.049	0.972	15.5	1.22	0.945	84
Cd	18.87	0.05	0.997	0.98	1.27	0.999	85

Adsorption kinetics: In the past decades, many mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. Both models are applied to describe the kinetic process of adsorption. However, they are quite different in nature⁸⁵.

At present, adsorption reaction models have been widely developed or employed to describe the adsorption kinetics⁸⁶. To develop sorption kinetics, knowledge of the rate law describing the sorption system, is required. The rate law is determined by experimentation and it cannot be inferred by mere examination of the overall chemical reaction equation⁸⁷.

The pseudo first-order kinetic equation is given as such equations⁸⁸:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t)$$

Where: q_e and q_t are the amount of adsorbed waste (mg/g) at equilibrium and at any instant of time t (min), respectively and k_1 is the rate constant of pseudo first order adsorption operation (min^{-1})⁸⁹.

The pseudo second order kinetic equation is given as such equation:

$$\frac{dq_t}{dt} = k (q_e - q_t)^2$$

Where: q_e and q_t are the sorption capacity at equilibrium and at time t , k is the rate constant of pseudo second.

Intraparticle Diffusion Model:

The adsorption process requires a multi-step approach involving the transport of solute molecules from the aqueous phase to the surface of the solid particles, followed by diffusion of the solute molecules into the interior of the pores, which is likely to be a slow process. The rate constant for intra-particle diffusion (k_{id}) is given by Weber and Morris⁹⁰.

$$q_t = k_{id} \cdot t^{1/2}$$

Where: q_t is the amount adsorbed (mg g^{-1}) at time t (min), k_{id} is the intraparticle diffusion coefficient.

Conclusion

In recent years, increasing cost and environmental considerations associated with the use of commercial adsorbents has led to development of low cost adsorbents derived from renewable resources. A review of fly ash as an adsorbent presented in this paper shows the chemical composition of coal fly ash, toxicity and sources of heavy metals in wastewater. Summary of fly ash for the removal of heavy metal ions, batch studies on the parameter that affects the adsorption, adsorption modeling such as isotherm, kinetics and thermodynamics. The use of waste materials as low cost adsorbents for removing various pollutants from wastewater presents many features especially their contribution in the reduction of cost for waste disposal, therefore contributing to environmental protection. More studies should be carried out for a better understanding of the process of low cost adsorption instead of promoting the use of non-conventional adsorbents on a large scale.

References

- 1 Nurliyana Ariffin, Mohd Mustafa Al Bakri Abdullah, Mohd Remy Rozainy Mohd Arif Zainol, Mohd Fared Murshed, Hariz-Zain, Meor Ahmad Faris and RIDHO Bayuaji. Review on Adsorption of Heavy Metal in Wastewater by Using Geopolymer, MATEC Web of Conferences 97,01023 (2017).
- 2 Shah Jyoti, Kumar sanjeev, Sharma Sudha and Sharma Rajeev, Sharma Rupinder. Removal of Nickel from aqueous solution by using low cost adsorbents: A Review, IJSEAS vol. - 2, issue-7 ,(2016).
- 3 M. Ghaedi, N. Mosallanejad. Removal of Heavy Metal Ions from Polluted Waters by Using of Low Cost Adsorbents: Review, J. of che. Health Risks 3(1) 7-22, (2013).
- 4 Singh B. K. and Nema Pragya. Characterization of Various Flyash fractions for Adsorption processes, Resaerch J. of Material sci.Vol.3 (3), 7-16, (2015).
- 5 Varma V. Geetha, Singh Ram Karan and Sahu Vaishali.A comparative study on the removal of heavy metals by adsorption using fly ash and sludge: A review. IJAIEM, Vol 2, Issue-7, 45-55 (2013).
- 6 Pandian N.S. Fly ash characterization with reference to geotechnical applications. Indian Inst.Sci. 84,189-216 (2004).
- 7 Visa Maria, Duta Anca. Cadmium and nickel removal from wastewater using modified fly ash: Thermodynamic and kinetic study. Scientific study & research, 73-82, (2008).
- 8 Majlinda N Daci, Nexhat M. Daci, Lulzim Zeneli, Salih T. Gashi, Dafina Hoxha.(2010).
- 9 Omar E. Abdel Salam, Neama A. Reiad, Maha M. Elshafei. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. J.of Advanced Research, 2,297-303,(2011).
- 10 Tena sijakova-Ivanova, Zoran Panov, Krsto Blazev, Vesna Zajkova-Paneva. Investigation of fly ash heavy metals content and physic chemical properties from thermal power plant, republic of Macedonia. IJEST, 3, 8219-8225. (2011).
- 11 Kipcak A.S., Acarali Baran N., Kolemen S.,Tugrul N.,Derun Moroydor E., Piskin S. Study on characterization of tuncbilek fly ash. Int. J. of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering. Vol. 6 No. 7, (2012).
- 12 Dwivedi M.K., Tripathi I.P., Dwivedi Kumar Atul, Removal of Cadmium from Wastewater Using Coal Fly Ash. Indian Journal of Applied Research, Vol.4, Issue 10, (2014).
- 13 Avirneni Sahithi, Bandlamudi Dharmateja. Environmental impact of thermal power plant in india and its mitigation measure. IJMERE, Vol.3, Issue.2, pp-1026-1031,(2013).
- 14 Agarwal Ajay K., Kadu Mahendra S., Pandhurnekar Chandrashekar P., Muthreja Ishwerdas L. Kinetics and adsorption isotherm study of removal of Zn²⁺ ions from aqueous solution using thermal power plant fly ash. Int. J. of Envir. Sc. And development, Vol. 3 No. 4, (2012).
- 15 Moyo M., Mugunil L., Nyamunda B.C. Optimisation of copper and zinc ions removal from aqueous solution by coal fly ash as an adsorbent. IJEST Vol. 4 No. 04, 2012.
- 16 Hajarnavis M R, Bhide A D. Removal of copper by adsorption on fly ash.j. of Scientific & Indus. Research. Vol. 60, PP 564-573. (2001).
- 17 Agarwal Ajay K., Kadu Mahendra S., Pandhurnekar Chandrashekar P., Muthreja Ishwerdas L. Characterization of coal fly ash and its ability to remove Ni²⁺ ions from aqueous solution. The holistic approach to environment 4, 17-29, (2014).

18 Shaobin Wang, Mehdi Soudi, Li Li, Z.H. Zhu. Coal ash conversion into effective adsorbents for removal of heavy metals and dyes from wastewater.(2005).

19 Hamedreja Javadian, Forough Ghorbani, Habib-allah Tayebi. Study of the adsorption of Cd (II) from aqueous solutions using zeolite-based geopolymer, synthesized from coal fly ash kinetic, isotherm and thermodynamic studies, Arabian j. of che. 8, 837-849, (2015).

20 Safaa M. Ragheb. Phosphate removal from aqueous solution using slag and fly ash. HBRC J. 9, 270-275,(2013).

21 Eleonora Soco, Jan Kalembkiewicz. Removal of copper (II) and zinc(II) ions from aqueous solution by chemical treatment of coal fly ash. Croat. Chem. Acta, 8893, 267-279. (2015).

22 Paulina Halas, Dorota Kolodynska, Agata Plaza, Marzena Geca and Zbigniew Hubicki. Modified fly ash and zeolites as an effective adsorbent for metal ions from aqueous solution. Adsor. Sci. Tech. Vol. 35(5-6) 519-533, (2017).

23 Deniz Sanliyüksel Yucel. Removal of heavy metals from aqueous solution using fly ash:can thermal power plant, NW Turkey as a case study. Karelmas Fenve Muh. Derg. 7(1):291-298, (2017).

24 Khairul Nizar Ismail, Kamarudin Hussin , Mohd Sobri Idris. Physical, chemical & mineralogical properties of fly ash. J. of Nuclear and related technology Vol. 4,47-51. (2017).

25 Nurcan Tugrul, Nil Baran Acarali, Seyma Kolemen, Emek Moroydor Derun, Sabriye Piskin. Characterization of catagzi fly ash for heavy metal adsorption. Int. J. of Chemical, molecular, nuclear, materials and metallurgical Engineering Vol: 6, No: 11, (2012).

26 Baig, M. Arif Ali, Sivapullaiah. Low cost adsorbents for heavy metal removal.Indian Geotechnical Con., 16-18 (2010).

27 Hala Ahmed Hegazi. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents, HBRC journal, 276-282,(2013).

28 Agarwal Ajay K., Kadu Mahendra S., Pandhurnekar Chandrashekar P., Muthreja Ishwerdas L. Removal of nickel (II) ions from aqueous solution using thermal power plant fly ash as a low cost adsorbent. Int.J of Envir.Protection, Vol. 3 Iss. 3, PP. 33-43(2013).

29 E. Tugcan TUZCU, Mustafa Umit ATALAY. Material characterizations and copper, zinc, and lead removing capacity of cayirhan fly ash. Turkish J. Eng. Env. Sci. 35, 93 – 105 (2011).

30 S Ram Mohan Rao and V. V. Basava Rao. Removal of hexavalent chromium from electroplating industrial effluents by using hydrothermally treated fly ash, J. of app. Sci. 7915, 2088-2092, (2007).

31 Maria Visa. Heavy metals removal on dye – modified fly ash substrateConference, 2011.

32 Paithankar Deepak Narayan, Kokate Vishvajit Bhaskar, Chaudhari Vishal Sadashiv. Removal of heavy metals from synthetic wastewater using peanut husk charcoal, fly ash and zeolite as adsorbents. IJMTER, (2015).

33 Widi Astuti, Agus Prasetya, Endang Tri Wahyuni, I Made Bendiyasa. The adsorption of lead from aqueous solutions using coal fly ash: Effect of crystallinity.Int.J. of Che., Mole., Nuclear and Metallurgical Eng. Vol-5, No-6, (2011).

34 K. S. Hui, Christopher Y H Chao. Removal of mixed heavy metal ions in wastewater by zeolite 4 A and residual products from recycled coal fly ash,Journal of Hazardous Material B 127,89-101 (2005).

- 35 Ishwardas L. Mutherja, Ajay K. Agarwal. Adsorption and kinetic behavior of fly ash used for the removal of lead from an aqueous solution, *J. of che. tech. and metallurgy.* 52, 3,505-512 (2017).
- 36 Yang Dong, Jinder Jow, Jianhui Su and Shin-Yaw Lai. Fly ash separation technology and its potential applications.
- 37 Srivastava S.K., Verma N., Das T.B. and Das Rupa. Removal of zinc from waste water by adsorption on flyash, *IJEP* 27 (6),502- 508 (2007).
- 38 Kannan N., Kanimozhi R. and Xavier A. Studies on the removal of mercury (II) – EDTA complex by coal and coal-flyash blends, *IJEP* 30 (9), 719-724 (2010).
- 39 Maria Harja, Lacramioara RUSU, Daniel BUCUR, Corneiuu MUNTEANU, Ramona Carla CIOCINTA. Fly ash-derived zeolites as adsorbents for Ni removal from waste water. *Rev. Roum. Chim.*, 57(6), 587-597 (2012),.
- 40 Murat KILIC, Ozge CEPELIOGULLAR, Cisem KIRBIYIK, Ersan PUTUN, Ayes E. PUTUN. Utilization of coal fly ash as low-cost adsorbent material for nickel removal application, *Anadolu univ. J. of sci. and tech.* 15 (2), (2014).
- 41 Chih-huang Weng, C.P. huang. Adsorption characteristics of Zn (II) from dilute aqueous solution by fly ash.
- 42 Robert M. Brooks, Mozghan Bahadory, Fernando Tovia, Hossein Rostami, *Int. j. of soil, sediment and water*, vol.3, issue. 2, Article 14.
- 43 LIU Zhuannian, WANG Guirong, ZHAO Xiaoguang. Removal of Cr (VI) from Aqueous solution using ultra coal fly ash. *Journal of wuhan university of Technology- Mater.Sci.Ed.* Apr.(2010).
- 44 Mohammad Sajid Ansari, Azizulhasan Ansari, Bhat Bilal Bashir, Abdulaziz Ansari. Studies on Adsorption Behaviour of Heavy Metals on Mixture of Fly ash and sand for their Removal of Heavy Metals from Textile Effluent. *Ultra Chemistry* Vol.10(1).49-69 (2014).
- 45 Thaligai Subramanian Malarvizhi, Thirumalai Samy Santhi. Demineralised lignite fly ash for the Removal of Zn (II) ions from Aqueous solution, *Journal of Water Resource and Protection.* 5,72-81(2013).
- 46 Alka Pradhan and Jitendra P. Deshmukh. Utilization of fly ash for Treatment of acid mine water. *J. of Environmental Research and Development*, Vol-3 No.1, July-September (2008).
- 47 Ting-chu Hsu. Adsorption of an acid dye on to coal fly ash. *Fuel* 87, 3040-3045, (2008).
- 48 Suwan Chaiyasith, Pachernchai Chaiyasith and Chutima Septum. Removal of Cadmium and Nickel from Aqueous Solution by Adsorption on to Treated fly ash from Thailand. *Thammasat Int.J.Sc.Tech.*, Vol-11, No.2, April-June (2006).
- 49 H.Polat, A.Vengosh, I.Pankratov, M.Polat. A New Methodology for removal of boron from water by coal fly ash. *Desalination* 164, 173-188 (2004).
- 50 Parag solanki, Vikal Gupta and Ruchi Kulshreatha. Synthesis of Zeolite from fly ash and Removal of heavy metals ions from Newly Synthesized zeolite. *e-journals.net.* 7(4), 1200-1205 (2010).
- 51 Krishna Gopal Ghosh, Kaustuv Mukherjee, Sunil Saha, FLY ASH OF THERMAL POWER PLANTS: REVIEW OF THE PROBLEMS AND MANAGEMENT OPTIONS WITH SPECIAL REFERENCE TO THE BAKRESHWAR THERMAL POWER PLANT, EASTERN INDIA, *International Journal of Geology*,

52 M.K. Dwivedi¹, Neeraj Jain, Pragati Sharma, Chanchala Alawa, Adsorption of Safranin from Wastewater Using Coal Fly Ash, IOSR Journal of Applied Chemistry (IOSR-JAC) e-ISSN: 2278-5736. Volume 8, Issue 4 Ver. II (Apr. 2015), PP27-35 www.iosrjournals.org.

53 Liangliang Wei¹, Kun Wang, Qingliang Zhao, Chunmei Xie¹, Wei Qiu¹, Ting Jia, Kinetics and equilibrium of adsorption of dissolved organic matter fractions from secondary effluent by fly ash, Journal of Environmental Sciences 2011, 23(7) 1057–1065, www.sciencedirect.com.

54 Min-Gyu Le^C, Gyeong beom Yi, Byoung-Joon Ahn, Felicity Roddick, Conversion of coal fly ash in to zeolite and heavy metals removal characteristics of the products, Korean J. Chem. Eng., 17(3), 325-331 (2000)

55 Tripathi Aushutosh and Rawat Ranjan Manju. Heavy metal removal from wastewater using low cost adsorbents, JBRBD vol. 6, issue 6, (2015).

56 Haaris Ahsan Safdari and Mohd Kaifiyan. Biosorption of Lead (II) AND Nickel (II) From Dilute Aqueous Solution Using Fly Ash as a Biosorbent. Vol-5, (3) 65-70 (2017).

57 Siti Nur Aaisyah Abas, Mohd Halim Shah Ismail, Md Lias Kamal and Shamsul Izhar. Adsorption Process of Heavy Metals by Low-Cost Adsorbent: A Review. World Applied Science J. 28(11) 1518-1530, (2013).

58 P. Rajesh Kumar, P. Akila Swathanthra, V.v.V. Basava Rao and S. Ram Mohan Rao. Adsorption of cadmium and zinc ions from aqueous solution using low cost adsorbents, J. of app. Sci. 14 (13): 1372-1378, (2014). izens, Issue 15 March 2009.

59 M .Vasanthi, M. Sangeetha and R. kalaiselvi. A comparative study on the chromium removal efficiency of flyash and commercial activated carbon, Jr. of ind. Poll. Control 20 (1) pp. 37-44 (2004).

60 S. Sheeba Thavamani, D. karthika Navaneetha. A comparative study of fly ash and Na-fly ash as adsorbents for removal of Cr (VI), Cu(II) and Fe(II) from aqueous solutions. IJARIT Vol. 3, Issue 4, (2017).

61 Pahade Vinod, Sharma Dr. A.K. Manganese removal by low cost adsorbent from synthetic wastewater- A review. Int.J. of Eng. Research Vol No. 4, Issue No. 3, PP-111-114.

62 Evans T. Musapatika, Maurice S. Onyango, Ochieng Aoyi. Research Article, vol-106, No. 9/10. <http://www.sajs.co.za>.

63 Amaresh, N.P. Hoolikantimath. Removal of chromium from synthetic wastewater using adsorption technique, IRJET vol. 2, issue-6, (2015).

64 Abinaya R., Hemapriya g., Dhinesh Kumar S. Removal of chromium from tannery effluent using flyash, IJIRD vol. 4, issue-4, (2015).

65 Dr. V. chitradevi, S. Mothi. Kinetics study of Cr(III) adsorption onto low cost fly ash adsorbent, IJERGS, vol. 3, issue-2, (2015).

66 Tyagi Pankaj Kumar. Study of potentiality of coal fly ash for the removal of Cr (VI) from industrial wastewater: Equilibrium and kinetic studies, IJETSR vol. 4, issue 8, (2017).

67 A.A. Lole, V.V. Patil, S.B. Patil, D.A. Gunjagi, N.U. Bavane. Optimization of copper ion removal from wastewater by using coal fly ash. IJRASET Vol. 4 Issue XII, 2016.

68 Chandra Irawan, Atikah, and Barlah Rumhayati. Adsorption of iron(II) by fly ash adsorption from coal, J. pure app. Chem. Res.,393, 88-98. (2014).

69 Eko Prasetyo Kuncoro, Mochammad Zakki Fahmi. Kinetics of Hg and Pb removal in aqueous solution using coal fly ash adsorbent. IPTEK, Vol. 25, No. 3, (2014).

70 V. Sridevi, M.V.V.Chandana Lakshmi, Satya vani Yadla. Adsorption isotherm studies of lead from aqueous solution using fly ash. Int. J. of Innovative research in Sci., Engineering and Tech. Vol. 2, Issue 11, (2013).

71 Agarwal Ajay K., Kadu Mahendra S., Pandhurnekar Chandrashekar P., Muthreja Ishwerdas L. Langmuir, Freundlich and BET adsorption isotherm studies for zinc ions onto coal fly ash. IJAIEM Vol. 3, Issue 1, (2014).

72 Sharma Y.C., Uma, Singh S.N., Paras, Gode F. Fly ash for the removal of Mn(II) from aqueous solutions and wastewaters. Che. Engineering J. 132, 319-323 (2007).

73 Gupta V.K.,Sharma S.,I Removal of Zinc from Aqueous Solutions Using Bagasse Fly Ash - A Low Cost Adsorbent(Article), Industrial and Engineering Chemistry Research,Volume 42, Issue 25, 10 December 2003, Pages 6619-6624 .

74 Song huiping, Cheng Huaigang, Zhang Zepeng and Cheng Fangqin, Adsorption properties of Zeolites Synthesized from coal fly ash for Cu (II), Journal of Environmental Biology, www.jeb.co.in.

75 Thaligai Subramanian Malarvizhi, Thirumalaisamy Santhi, Demineralised Lignite Fly Ash for the Removal of Zn(II) Ions from Aqueous Solution, Journal of Water Resource and Protection, 2013, 5, 72-81 <http://dx.doi.org/10.4236/jwarp.2013>.

76 Lita Darmayanti, Suprihanto Notodarmodjo, Enri Damanhuri, Removal of Copper (II) Ions in Aqueous Solutions by Sorption onto Fly Ash, J. Eng. Technol. Sci., Vol. 49 No. 4, 2017, 546-559.

77 T. S. Malarvizhi, T.Santh, Lignite fired fly ash modified by chemical treatment for adsorption of zinc from aqueous solution, Res Chem Intermed 2013 39:2473–2494.

78 Justyna Ulatowska, Izabela Polowczyk, Wojciech Sawiński, Anna Bastrzyk, Tomasz Koźlecki, Zygmunt Sadowski, Use of fly ash and fly ash agglomerates for As(III) adsorption from aqueous solution, Pol. J. Chem. Tech., Vol. 16, No. 1, 2014 ,21-27.

79 Suresh Gupta, B V Babub, Removal of Cr(VI) from Wastewater using Fly ash as an Adsorbent, Article · January 2008,<https://www.researchgate.net/publication/237426144>

80 Febrianto, J., A.N. Kosasih, J. Sunarso, Y. Ju N. Indraswati and S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. Journal of Hazardous Materials, 162,616-645, (2009).

81 Chi-Chuan Kan, Aldwin H. Ibe , Kim Katrina P. Rivera , Renato O. Arazo ,Mark Daniel G. de Luna , Hexavalent chromium removal from aqueous solution by adsorbents synthesized from groundwater treatment residuals, Sustainable Environment Research 27 (2017) 163e171, journal homepage: www.journals.elsevier.com/sustainableenvironment-research/

82 Goswami A.K.,Kulkarni S.J.,Dharmadhikari S.K.,Phutke Minakshee.Adsorption of Cu(II) ions from synthetic waste water by fly ash.IJSETR,Vol 2 (6),June (2013).

83 Ashfaq Ahmad, Ali,Anwar,Goel Ritesh,Ram Sobha.Removal of Nickel from Aqueous solution using fly ash: Equilibrium and kinetic studies,(ICLTESHM) (2017),www.conference world.

- 84 Malarvizhi T.S., Lignite fired fly ash modified by chemical treatment for adsorption of Zn from Aqueous solution. Vol 39,(06), pp 2473-2494, (2013).
- 85 Ulatowska Justyna, Polowczyk Izabela, Sawinski Wojciech, Bastrzyk Anna, Kozlecki Tomasz, Sadowski Zygmunt. Use of fly ash and fly ash agglomerates for As (III) Adsorption from Aqueous Solution. Polish J. of chemical Tec., (2014).
- 86 Arash Borzou, Mahmoud Kalbasia, Mehran Hoodajia, Majid Abdoussb, Ahmad Mohammadia, Isotherm investigation of the adsorption of cadmium onto modified poly(ethylene terephthalate) fiber, European Journal of Experimental Biology, 2014, 4(2):136-142, www.pelagiaresearchlibrary.com.
- 87 Visa Maria, Nacu Mihaela, Carcel Adrian Radu. Fly ash Substrates for complex wastewater Treatment, (WOCA) conference, (2011).
- 88 S.A.S. Mohammed, N. Maya, A Review and Evaluation of Selected Kinetic Models and Sorption Processes in Amended Soils, International J. of Research in Chemistry and Environment, 1,2, (2011).
- 89 S.A.F. Banat, L. Abu-Allah, Adsorption of Phenol using different types of activated bentonites, Separation and Purification Technology, 35, 11-10, (2003).
- 90 Agarwal Ajay K., Kadu Mahendra S., Pandhurnekar Chandrashekar P., Muthreja Ishwerdas. Kinetics study of the adsorption of Ni²⁺ ions onto fly ash, J. of che. tech. and metallurgy, 50, 5, 601-605 (2015).
- 91 Oyaro, N., O. Juddy, E.N.M. Murago and E. Gitonga, 2007. The contents of Pb, Cu, Zn and Cd in Nairobi, Kenya. Journal of Food Agriculture Environment, 5(3-4): 119-121.
- 92 Khaled, A., A.E. Nemr, A. El Sikaily and O. Abdelwahab,. Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon. Desalination 210-232 (2009).
- 93 T.S. Anirudhan, K.P. Shubha, C. Raji, Immobilization of heavy metals from aqueous solution using polyacrylamide grafted hydrous tin(VI) oxide gel having carboxylate functional groups, Water Research, 35, 300-310, (2001).