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Elimination of heavy metals and pesticides from wastewater by using Bagasse Fly Ash

Haroon Ejaz[1], Qaisar Mehmood Saharan*[,1], Salman Ashiq[1]

[1]*Researchers, Department of Chemistry, Lahore Garrison University, Lahore, Punjab, Pakistan*

***Corresponding Author:** *Qaisar Mehmood Saharan, Researcher, Department of Chemistry, Lahore Garrison University, Lahore, Punjab, Pakistan; Email: qaisarmehmood4114@gmail.com, Mob: +92311-0144114*

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ABSTRACT

Bagasse Fly Ash (BFA) is a rejected material of bagasse that is produced in the sugar industry after burning as a fuel. After this discovery, it is used as a cheap, effective and more reliable adsorbent with the highest elimination rate than activated carbon for various harmful heavy metals and pesticides at different factors like pH, contact time, adsorbent dose, adsorbate concentration, temperature, particle size by Batch and column studies. Various factors established the results at a slight change in adsorbent concentration. Pesticides and heavy metals have more adverse effects on human health as well as on the water bodies organisms like many systems as reproduction, urinary, neurological, circulatory, digestive, soil fertility fluctuations as acidity and basicity. Both this substance is discharged directly or indirectly into water bodies and soil by the anthropogenic activities done in industrial as well as agricultural fields. Various techniques were utilized for the elimination of heavy metals and pesticides in the past with high expenses as well as difficult to manage. But in future, this review may help in new efficient adsorbent with high removal ability at a low price as well as easy to use than others adsorbents for the elimination of harmful heavy metals and pesticides from wastewater.
Keywords: Bagasse fly ash; adsorption metals ions copper; zinc; lead; column studies; chromium; nickel; DDE; DDD; lindane; malathion; Methyl parathion; selenium; wastewater; cadmium.

INTRODUCTION

Pesticides are natural or synthetic substances that are used on agricultural land to kill or retard the growth of pests, [1] weed and diseases by these crops can be protected and get more and better yield for the storage, supplies to the food chain dependent. [2, 4] In 1867, the first chemical pesticide was synthesized in the USA that name is Paris green. [5] Then in the 19th century, US farmers started to used nicotine sulfate, sulfur, calcium arsenate to overcome the power of pests in field crops except for Paris green. [6] After this in the middle of the 20th century, these synthetic chemical substances were mostly used for pests controlling. [7, 8] So, it can be categorised either by target pests such as insecticides, herbicides, and fungicides or by chemical identity mean variable levels of toxicity. [9, 10] One class is organochlorine insecticides which are composed of carbon, hydrogen, and chlorine can attack the CNS by this insect neuro cells start to damage and

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become paralysis and by suffocation death may occur [11] while the second class is organo-phosphates that are the derivatives of phosphoric acid which are extremely toxic pesticides which consist on a phosphate group that participate probably 48.6% of all pesticides in 1997. [12]

As organophosphates are easily decomposed than organochlorines but there is a great threat to the ecosystem due to its acute toxicities within seconds, minutes or hours after exposure by inhalation, ingestion and dermal contacts to mammalian health like cancers (non-Hodgkin's lymphoma), leukaemia, body tissue, autoimmune disease, reproductive abnormalities and different kind of solid tumours. [10, 13-18] Because of the presence of harmful substances like DDTs, gamma-HCH, aldrin and diazinon that has some adverse effects when combining with different substances and become persistent for the environment. [19-24] Hence there is an approximal range of less than 0.1% of pesticides that utilizing the farmland to reaches the substrate. Some portion of pesticides remains in farmland while some extent becomes a part of surrounding surface water like organochlorine insecticides by runoff from agricultural lands and had an adverse effect on lake biological communities that forcefully changes from clear water state to dirty water state by affected zooplankton about thirty years after used than had been banned. [10, 25-30] The toxicity and division of pesticides shown by WHO [31] in LD_{50} value that is present in mg of pesticide/kg of body weight of the interested animal and its value range from > 0.1 to < 5000.

According to Csuros and Csuros [32] "Heavy metals are those metals that have more than 40.04 (Ca) atomic weight [33] and more than 5 g/cm^3 density" and also an adverse effect on the ecosystem. [34] The most detected heavy metals in wastewater contain As, Cd, Cr, Cu, Pb, Ni and Zn, Hg, Se. [35] These metals enter the surroundings by natural changes in the earth's crust, volcanic eruptions and anthropogenic activities [36] including soil erosion, natural, mining, industrial effluents (Tanning, Electro-plating),urbanization, runoff, sewage discharge and some others. [37-39] Heavy metals become persistent for the environment, food chains, therefore arises various health issues due to their toxic effects. [40]

In the past, accidentally exposure of these metals in 1932 Minamata and Itai-Itai were caused by consumption of Hg-contaminated fish and Cd-contaminated rice, respectively. Its contamination quantity is increasing day by day in South-East Asia like India, Thailand and China. [41, 42] There are several symptoms disclose due to the exposure of heavy metals (cadmium, lead, zinc, Ni, As and Hg) on central nervous system disorders, kidney infections, liver problems, depression, vision disability, insomnia, constipation. [40, 43-46] The trace concentrations range of heavy metals from 1ppb to less than 10ppm in different environmental systems. [47] Both pesticides and heavy metals become more adverse for human health when crossing specific ranges. For the safety of human health, the food chain should be checked routinely for bioaccumulation due to the presence of heavy metals and pesticides. [48, 49] During municipal and industrial activities some adequate treatments should be used before discharging the waste-waters into natural ecosystems. [50] But unfortunately, cheap treatment is not available especially in developed countries. [51, 52]

Sugarcane bagasse fly ash is a burning residue of bagasse that is obtained from the boiler chambers of the sugar industry. [53] Firstly, A huge amount of sugarcane (*Saccharum officinarum*) is growing in Brazil at 672.16 while secondly India 285.03 million tons in all over the world. [54, 55] The chemical composition of bagasse fly ash SiO_2-60.5%; Al_2O_3-15.4%; CaO-2.90%, Fe_2O_3-4.90%, MgO-0.81% also the presence of mullite, hematite, kaolinite, 3-quartz, gamma-alumina and geolite was suggested by the X-ray diffraction pattern of the bagasse fly ash 'd' spacing values. [56] More studies about the utilizing of sugarcane bagasse fly ash are non-cohesive material having a low specific gravity that acts as an activator with cheap and more efficient for the adsorption of heavy metals after acidic treatment 53% to 88%. [57-59] There are several methods like reduction, ion exchange, precipitation, reverse osmosis, electrodialysis, adsorption, reduction, coprecipitation, solvent extraction that could be used for the removal of heavy metals and pesticides, however, adsorption is the most widely used method for the management of heavy metals poisoning and pesticides ingestion. [56, 60-65]

Discussion about removal of Heavy Metals

Cadmium

According to ATSDR ranking, Cd lies on 7th with its toxicity level and formed during zinc production as a by-product. During WW1, cadmium was utilized as a substitute for Tin whereas in paint industries as a pigment agent. [66] As an environmental exposure of Cd in China and Japan than other countries. [67] So, the researcher needs an effective and cheap method for the removal of Cd. 90% cadmium is adsorbed by preparing the relative solution of cadmium nitrate in deionized water within a series of Erlenmeyer flasks of 100 ml with bagasse fly ash adsorbent during batch phenomena. In the case of cadmium heavy metal, its adsorption by adsorbent is discussed at various factors. A Langmuir is superior to the Freundlich model while Q_o is the Langmuir constants related to maximum adsorption capacity. The adsorption rate of Cd is proportional to the temperature, if the temperature increased then adsorption also increased it indicates the adsorption process is endothermic in nature (Table 1).[56, 68]

Table 1. Characteristics of Cadmium

	pH of solution max	Adsorbent dose max	Adsorbate concentration max	Temperature max	Particle size max	Contact time Max	Langmuir constants Q_o(mg/g)		Freundlich constants K_F		Experiment mode	Reference
Cd	6.0	10 g l^{-1}	14 mgl^{-1}	50°C	100–150 µm	60 min	30°C	1.24	30°C	1.02	Batch	56
							40°C	1.67	40°C	1.11		
							50°C	2.00	50°C	1.26		

Nickel

90% nickel is removed from wastewater by the use of bagasse fly ash that acts as a cheap and efficient adsorbent under the testing process. Batch phenomena are carried out by the preparation of Nickel nitrate ($NiNO_3$) solution in deionized water within a series of Erlenmeyer flasks of 100ml. The bagasse fly ash (BFA) exhibits better adsorption capacity than activated carbon and the sorption data is arranged by Langmuir and Freundlich. In the case of nickel Langmuir is best than the Freundlich model while Q_o is the Langmuir constants related to maximum adsorption capacity. The adsorption rate of Ni is directly proportional to the temperature, if the temperature increased then adsorption also increased it's mean the adsorption process is endothermic in nature (Table 2). [56]

Table 2. Characteristics of Nickel

	pH of solution max	Adsorbent dose max	Adsorbate concentration max	Temperature max	Particle size max	Contact time Max	Langmuir constants Q_o(mg/g)		Freundlich constants K_F		Experiment mode	Reference
Ni	6.5	10 g l^{-1}	12 mgl^{-1}	50°C	100–150 µm	80 min	30°C	1.12	30°C	0.90	Batch	56
							40°C	1.35	40°C	1.05		
							50°C	1.70	50°C	1.17		

Copper

In the case of copper heavy metal, its adsorption is done nearly 90-95% by the low price as well as more efficient adsorbent known as bagasse fly ash. Therefore, an aqueous solution of copper sulphate is used for this estimation to get results of various parameters. Column studies give more efficient results about the Cu removal through BFA at 15 parts per million. Their final results indicate that this procedure has endothermic nature (Table 3). [46]

Table 3. Characteristics of Copper

	pH of solution max	Adsorbent dose max	Adsorbate concentration max	Temperature max	Particle size max	Contact time	Langmuir constants Q_o(mg/g)		Freundlich constants K_F		Experiment mode	Reference
Cu (II)	4.0	10 g/l	2.30 mg/g	30°C	200–250 µm	60 min	30°C	2.26	30°C	2.14	Batch, Column studies 0.50 ml/min	46
							40°C	2.34	40°C	2.09		
							50°C	2.36	50°C	2.04		

Zinc

Nearly 90 to 95% Zn is adsorbed by the cheap and more compatible activator adsorbent as BFA in batch and column studies by preparing the solution at15-ppm of zinc sulphate with double distilled water equipped with Erlenmeyer flasks of 50 ml. The main advantage of column studies that can be regenerate and recover after being used with different eluents at least 10 times with 93-98% removal of Zn metal. Both metals sorption data are followed by Langmuir and Freundlich models and exhibit endothermic nature (Table 4). [46]

Table 4. Characteristics of Zinc

	pH of solution max	Adsorbent dose max	Adsorbate concentration max	Temperature Max	particle size max	Contact time	Langmuir constants Q_o(mg/g)		Freundlich constants K_F		Experiment mode	Reference
Zn (II)	5.0	10 g/l	2.35 mg/g	30°C	200–250 µm	75 min	30°C	2.34	30°C	2.37	Batch, Column studies 0.50 ml/min	46
							40°C	2.45	40°C	2.26		

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Lead (Pb^{2+})

According to the Indian Standard Institution (ISI), The bearable amount of lead in drinking water is 0.05 mg L^{-1} [69] while in the land surface water is 0.1 mg L^{-1}.[70] The test solution Pb $(NO_3)_2$ is prepared in double-distilled water for the analysis of lead in wastewater. The sorption study is followed by Langmuir and Freundlich and the final result of this determination is exothermic in nature TABLE 2.4. [65] Lead is a highly toxic metal that has various health problems in every habitat where living things are alive. In the US, more than 100 to two million lead is discharged via vehicle exhausts. Normally human exposure is due to food and drinking water[(71)]. About 96 to 98% lead is adsorbed by BFA during batch and column studies 95 to 96% with a flow rate of nearly 0.5 ml/min. Its final results disclose their behaviour which is exothermic in nature (Table 5). [45]

Table 5. Characteristics of Lead

	pH of solution max	**Adsorbent dose max**	**Adsorbate concentration max**	**Temperature Max**	**Particle size max**	**Contact time**	**Langmuir constants $Q_{o}\times10^3$ mg^{-1}**		**Freundlich constants K_F**		**Experiment mode**	**Reference**
Pb (II)	3.0	10 g/l	4.80 × 10^{-4} M	30°C	150–200 µm	6-8 hours	30°C	2.73	30°C	13.77	Batch	65
							40°C	1.54	40°C	11.75		
							50°C	1.38	50°C	9.66		

Chromium

Cr has the seventh number with respect to abundance on earth. [72] 96-98%Cr are removed by this use of inexpensive and more reluctant adsorbent material BFA while with column studies 95-96% at a flow rate about 0.5ml/min respectively. There is two most abundant form of chromium is present with oxidation state Cr^{3+} and Cr^{6+}has toxic to the ecosystem. [73] Results show it is exothermic in nature due to adsorption has an inverse relation with temperature (Table 6.1). [45] Potassium dichromate solution ($K_2Cr_2O_7$) is used for the adsorbent of Cr VI. This is exothermic in nature (Table 6.2). [74]

Table 6.1. Characteristics of Chromium

	pH of solution max	**Adsorbent dose max**	**Adsorbate concentration max**	**Temperature Max**	**Particle size max**	**Contact time**	**Langmuir constants $Q_{o}\times10^3$ mg^{-1}**		**Freundlich constants K_F**		**Experiment mode**	**Reference**
Cr	5.0	10 g/l	20 ppm	30°C	200–250 µm	60 min	30°C	4.35	30°C	1.86	Batch, Column studies 0.50mL/min	45
							40°C	3.30	40°C	1.75		
							50°C	4.25	50°C	1.66		

Table 6.2. Characteristics of Chromium

	pH of solution max	**Adsorbent dose max**	**Adsorbate concentration max**	**Temperature Max**	**Particle size max**	**Contact time**	**Langmuir constants $Q_{o}\times10^3$ mg^{-1}**		**Freundlich constants $K_F \times 10^4$**		**Experiment mode**	**Reference**
Cr (VI)	1.0	0.1 gl^{-1}	9.60 × 10^3 M	30°C	200–250 µm	60 min	30°C	5.00	30°C	6.33	Batch, Column studies 0.4 cm^3 min^{-1}	74
							40°C	2.38	40°C	1.99		

Zinc

It is a toxic metal that can be found in natural water bodies as well as in industrial wastes. Due to its metallic bitter taste, it can be categorized at secondary drinking water standard within 5.0 mg L^{-1}. [75] So, 2% zinc is required for the normal behaviour of DNA polymerization and also for protein preparation. Its solution is preparing within Zn $(NO_3)_2$ in doubly distilled water.it is exothermic in nature (Table 7). [76]

Table 7. Characteristics of Zinc

	pH of solution max	**Adsorbent dose max**	**Adsorbate concentration max**	**Temperature Max**	**Particle size max**	**Contact time**	**Langmuir constants $Q_{o}\times10^3$ mg^{-1}**		**Freundlich constants $K_F \times 10^4$**		**Experiment mode**	**Reference**
Zn^{2+}	4.0	10 g/l	1.22 × 10^{-3} M	30°C	150–200 µm	6-8 hours	30°C	2.02	30°C	3.10	Batch	76
							40°C	1.97	40°C	1.23		
							50°C	1.85	50°C	0.132		

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Arsenic Species

About 95.0 arsenates and 89.5 arsenite % can be adsorbed from wastewater by BFA in the Batch process while 98.9 and 95.6 % by column operations at a flow rate of 1.0 mL/min. According to WHO, the tolerated amount of (As) in groundwater is 10.0 μg/L. arsenic is present in two oxidation states such as As (V) and As (III). As become more harmful when is combined with inorganic than organic species. So, arsenite is more dangerous than arsenate. [77] The final result indicate it is exothermic in nature (Table 8). [78]

Table 8. Characteristics of Arsenic Species

	pH of solution max	Adsorbent dose max	Adsorbate concentration max		Temperature max	Particle size max	Contact time	Langmuir constants q_o (μg/g)		Freundlich constants K_F(μg/g)		Experiment mode	Reference
As species	7.0	3.0 g/L	As (V)	As (III)	20.0°C	150–200 μm	50.0 min	As (V)		As (V)		Batch	76
			80.0 μg/L	70.0 μg/L				20°C	19.763	20°C	9.6095		
								25°C	20.747	25°C	8.7036		
								30°C	18.868	30°C	8.1433		
								As (III)		As (III)			
								20°C	21.510	20°C	7.0437		
								25°C	20.921	25°C	6.6227		
								30°C	19.960	30°C	6.3503		

Selenium (IV)

According to the US(EPA), a standard amount is set for the drinking purpose of selenium is 0.05 mg/L. [79] But unfortunately, India crosses this range and become a great threat to the environment. Different conventional phenomena such as adsorption by ferrihydrite, catalyzed cementation, biological and enzymatic reduction are available for Se removal from wastewater in large treatment plants. Amorphous substances such as iron oxyhydroxide and MnO_2 were utilized for Se removal. [80] A solution is prepared by mixing with 0.1 M $FeCl_3$ for Se (IV) removal (Table 9). [81]

Table 9. Characteristics of Selenium

	pH of solution max	Adsorbent dose max	Adsorbate concentration max	Temperature max	Particle size max	Contact time	Langmuir constants q_o (μg/g)		Freundlich constants K_F(μg/g)		Experiment mode	Reference
Se (IV)	6.64	4 g/l	100 μg/L	293K	150–200 μm	2 hours	293	207.7156	293	7.32455	Batch	81
							303	176.2859	303	6.78278		
							313	158.936	313	6.29384		
							323	152.5316	323	6.12955		

Discussion about removal of Pesticides

Lindane

Lindane is a form of insecticide which is used for insect-killing that damage the texture of plants. Lindane is also used by forestry to keep the growth of pests under control. [82] It is a gamma isomer of HCH. It is used in therapeutic pesticides that control the lice and mites in human beings.[83] It can cause serious health problems like disrupting and damaging reproduction and CNS. [84] It is more soluble in an aqueous medium than other organochlorine compounds so become persistent in water bodies. This becomes a part of water by spraying it for the control of mosquitos by forestry but unfortunately level up to 43μg/l have been found in India[85]. The detection limit of lindane is 0.01 μgL^{-1}. [86, 87] So investigators need a more reliable and effective adsorbent that absorbed lindane from wastewater that became accidentally a part of water bodies. There are different parameters that effects on adsorption rate with batch and column study (Table 10). [88]

Table 10. Characteristics of Lindane

	pH of solution max	Adsorbent dose max	Adsorbate concentration max	Temperature max	Particle size max	Contact time	Langmuir constants Q_o (μg/g)		Freundlich constants K_F		Experiment mode	Reference
Lindane	6.0	5 g/l	2 μg/g	30°C	200–250 μm	60 min	30°C	2.51	30°C	1.91	Batch, Column studies 1.2 ml/min	88
							40°C	2.48	40°C	2.00		
							50°C	2.40	50°C	2.11		

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Malathion

Malathion is a class of organophosphate insecticide that was first time introduced by ACCR in 1956. It is mostly used to control mosquitoes, aphids. [89] On the behalf of EPA, only >1% malathion spray for mosquitoes killing. It is found in liquid form with yellow and garlic odour and become solidify below 37 °F. During 6 to 7 days malathion can be completely hydrolyzed. During the unfavourable condition, it becomes persist with a half-life range of about month to years while favourable range 7-14 days. [90] It has adverse effects on human health like gastrointestinal, dermal, CNS, respiratory. [88] So, to overcome these effects researchers need an effective method for the removal of malathion. The adsorption process is more effective for this removal than other techniques. During this removal, various factors effect on adsorption rate (Table 11). [88]

Table 11. Characteristics of Malathion

	pH of solution max	Adsorbent dose max	Adsorbate concentration max	Temperature max	Particle size max	Contact time	Langmuir constants Q_o(μg/g)		Freundlich constants K_F		Experiment mode	Reference
Malathion	6.0	5 g/l	2 μg/g	30°C	200–250 μm	60 min	30°C	2.08	30°C	1.81	Batch, Column studies 1.2 ml/min	88
							40°C	2.04	40°C	1.90		
							50°C	2.00	50°C	1.96		

Methyl Parathion

It is a member of organophosphorus insecticides that has harmful effects on human beings as well as animals such as neuroglial, reproductive, paralysis etc. [91] BFA is a more effective adsorbent with a high capacity of 44% than a rising husk, rice bran. This absorption result indicates that it is exothermic in nature (Table 12). [92]

Table 12. Characteristics of Methyl Parathion

	pH of solution max	Adsorbent dose max	Adsorbate concentration max	Temperature Max	Particle size max	Contact time	Langmuir constants Q_o $mmolg^{-1}$	Freundlich constants $mmolg^{-1}$	Experiment mode	Reference
Methyl Parathion	6.0	0.1 g	0.38×10^{-3}M	303K	200–250 μm	60 min	BFA	BFA	Batch	92
							0.39±0.005	5.4±1.4		

DDD and DDE

DDD and DDE are pesticides that are removed by BFA from wastewater. 93% by batch while 97-98% by column studies. The sorption study is followed Langmuir and Freundlich models that indicate it is exothermic in nature (Table 13). [93]

Table 13. Characteristics of DDD and DDE

	pH of solution max	Adsorbent dose max	Adsorbate concentration max	Temperature Max	Particle size max	Contact time	Langmuir constants Q_o(μg/g)		Freundlich constants K_F		Experiment mode	Reference
DDD	7.0	5 g/l	4.01 μg/g	30°C	200–250 μm	80 min	30°C	7.69	30°C	3.59	Batch, Column studies 0.50 ml/min	93
							40°C	7.61	40°C	3.52		
							50°C	7.54	50°C	3.47		
DDE	7.0	5 g/l	3.87 μg/g	30°C	200–250 μm	80 min	30°C	6.67	30°C	3.24	Batch, Column studies 0.50 ml/min	93
							40°C	6.60	40°C	3.19		
							50°C	6.53	50°C	3.12		

CONCLUSION

This review coined the high adsorbent capability of Bagasse fly ash which is obtained from the burning of bagasse in the sugar industry. From the environmental point of view, many adsorbents are utilizing for the adsorption of heavy metals and pesticides from the wastewater of many industrial and agricultural areas. BFA prove more efficient due to low price as well as easy to utilize for the detection of heavy metals and pesticides even at low ppb concentration than other expensive and low quantity adsorbent capacity like activated carbon or any other techniques. So, there are many parameters required which elaborate its final results. The main advantage of BFA is low-cost and suitable for column studies because the column can regenerate after being used.

Conflicts of Interest

All contributing authors declare no conflicts of interest.

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