Adsorption of Heavy Metals from Simulated Landfill Leachates unto Composite Mix of Agricultural Solid Wastes

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Abstract: *Leachates were simulated from decomposing solid waste soil samples obtained from two landfills in Kaduna metropolis the capital of Kaduna State in Nigeria. Three physicochemical properties and the concentration of heavy metals present in the simulated leachates were determined; adsorption studies using rice husk, sawdust and composite mix of both adsorbents were carried out on the simulated leachate. the heavy metal concentration of lead (0.53 to 1.07 mgL^{-1}), nickel (3.00 to 3.60 mgL^{-1}), cadmium (3.00 to 3.60 mgL^{-1}) and manganese (31.57 - 72.27 mgL^{-1}) exceeded the guideline limits for wastewater effluents set by the National Environmental Standards and Regulation Enforcement Agency. Sawdust is a more suitable adsorbent compared to rice husk in the removal of heavy metals from the simulated landfill leachate. Composite Mix 1 adsorbed more of the metals than Composite Mix 2 and 3 and it also adsorbed more of the heavy metals present in the leachate than rice husk and sawdust alone. Both Langmuir and Freundlich models were applicable to the adsorption of the metals studied and the experimental data were better described by the pseudo-second order kinetic model as evident from correlation coefficients.*

Keywords:*Adsorption, Heavy metal, Leachate and Agricultural Solid Waste.*

I. Introduction

Landfill is one of the most common methods for disposal of municipal solid waste around the world. After land filling, solid waste undergoes physicochemical and biological changes. The generation of leachate is caused principally by precipitation percolating through waste deposited in a landfill. Once in contact with decomposing solid waste, the percolating water becomes contaminated and flows out of the waste material [1]. As the liquidmoves through the landfill many organic and inorganic compounds, like heavy metals, are transported in the leachate. Leachate can be characterized as a complex mixture containing numerous inorganic as well as organic compounds.In Most urban and sub-urban areas in Nigeria, domestic and agricultural wastes are allowed to decompose in the open waste dumps. These open dumps do not have geo-liner or concrete walls that could prevent leachate from percolating in to the soil. Therefore, leachate generated by improperly located and managed solid waste disposal sites can destroy drinking water resources making it necessary to locate new sources, at considerable cost [2].

There are many methods for the removal of metal ions from solutions including, chemical precipitation, complexation, solvent extraction, and membrane processes. Adsorption processes have shown many advantages over these physicochemical methods. They are quite selective, effective, and are able to remove various levels of soluble heavy metals in solution [3].

In recent years, considerable attention has been focused on the removal of heavy metals using biosorbents. Raw agricultural solid wastes have been used as adsorbent. They are available in large quantities and have potential as sorbents due to their physicochemical characteristics and low cost. These agricultural solid wastes are readily available at negligible or no cost.

II. Materials And Methods

Kaduna metropolitan is the capital of Kaduna state and occupies the central portion of northern Nigeria. The dumpsites investigated are located at Airport/Lagos road (AD) at the outskirts of the metropolis and Malali-Water Works (MD) located within the metropolis (as shown in the map of Kaduna metropolis)

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fig. 1: Map of Kaduna Metropolis (Nigeria).

Key to dump sites:
AD: Airport/Lagos Road Dumpsite;MD: Malali Dumpsite

Sample Collection And Preparation:
Decomposing solid waste soil samples were collected randomly from twelve different points at a depth of 0 to 30 cm with a soil auger, mixed thoroughly to form bulk composite samples; samples were only taken from freshly exposed surfaces,kept in polythene bags and labeled [4]:

(i) AD: Airport/Lagos road Dumpsite (ii) MD: Malali Dumpsite.

These were then transported to the laboratory where the samples were air-dried.

Adsorbent:
Rice husk and sawdust waste were collected from local rice and timber mills and used as adsorbents in this study. The rice husk and sawdust were air dried, ground and sieved through a laboratory sieve of 2 mm diameter. With the exception of grinding and sieving no other pre-treatment of the rice husk and sawdust was made prior to the adsorption experiments [5].

Leachate Simulation:
Seven hundred grams of the decomposing solid waste soil samples into different 5 litre flasks. Exactly 2.8 litres of distilled water (four times the sample weight) was then added. The mixture was mixed thoroughly and allowed to stand for 48 hours at room temperature. Continuous stirring was done manually at intervals. After 48 hours the solid and liquid portions were separated first by decantation, and the liquid portions were then filtered with Whatman 540 filter paper to remove debris and stored at $4^{O}C$. The simulated leachates were then analyzed for heavy metals before the adsorption experiments [6].

Batch Experiments:
For the adsorption experiments rice husk, sawdust and composite mix of rice husk and saw dust [comprising Mix-1: 25% rice husk and 75% sawdust; Mix-2: 75% rice husk and 25% sawdust and Mix-3: 50% rice husk and 50% sawdust (weight by weight)] were used as adsorbents for the removal of heavy metals from the simulated leachates.

First Batch Experiment:
One gram of the adsorbent was weighed into a conical flask and 100 cm^3 of the simulated leachate added. The suspension was agitated at 250-rpm agitation speed with a Stuart Mechanical Shaker at room temperature for 2 hours and then filtered into a labelled 100 cm^3 plastic bottle through Whatman No. 540 filters paper to remove any suspended adsorbent and stored for elemental analysis [7].

Second Batch Experiment:
Batch sorption treatment was carried out with the ratio 1 g of adsorbent in 100 cm^3 of simulated leachate samples in different conical flasks. The suspensions in all sorption assays were agitated at 250 rpm agitation speed with a Stuart Mechanical Shaker at room temperature for various contact time, 't' (5, 10, 15, 20, 30, 45, and 60 minutes) [7 & 8].

Instrumentation:

Concentration of considered heavy metal ions was determined by a Bulk 210 Scientific Atomic Absorption Spectrophotometer Model 210 VGP, while the pH, conductivity and total dissolve solids (TDS) of the simulated leachate were measured with HACH pH, Conductivity and TDS meter respectively.

III. Results And Discussion

The simulated leachates varied form pale yellow to dark brown in colour. Physicochemical characteristics of the leachates depend primarily upon the waste composition and water content in the waste. The pale yellow to brown color of the simulated leachates is mainly attributed to the oxidation of ferrous to ferric form and the formation of ferric hydroxide colloids and complexes with fulvic / humic substances [9].

The results of pH, conductivity and total dissolved solids (TDS) of the simulated leachates from decomposing solid waste samples from the four investigated dumpsites is presented Table 1. The pH of the simulated leachates range from 8.41 to 8.60 moderately basic, were within the guideline limits for wastewater effluents set by National Environmental Standards and Regulations Enforcement Agency (NESREA).

Table 1: Some Physicochemical properties of simulated leachate

DUMPSITE	PHYSICOCHEMICAL PROPERTY		
	pH	CONDUCTIVITY (mScm^{-1})	TDS (gL^{-1})
AD	8.60± 0.26	3.76± 0.05	1.88± 0.04
MD	8.41± 0.03	2.48± 0.13	1.24± 0.04
NESREA, 2007	6 − 9	-	2.00

Total dissolved solids (TDS) of the simulated leachate samples range from 1.24 gL^{-1} to 1.88gL^{-1}. All the simulated leachates samples have values below the guideline limits for wastewater effluents set by National Environmental Standards and Regulations Enforcement Agency [10]. Conductivity of the simulated leachates samples range from 2.48 mScm^{-1} to 3.76 mScm^{-1}. Even though NESREA limits do not include electrical conductivity, the values obtained for the leachate samples were obviously high for wastewater effluent. The relatively high values of electrical conductivity indicate the presence of inorganic substances in the leachate samples.

Landfill leachate contains a variety of chemical agents, and their interaction and reactions under changing environmental condition further complicate the issue [11]. The concentration of cobalt, copper, chromium and iron range from 0.50 to 0.51mgL^{-1}, 0.52 to 0.95 mgL^{-1}, 0.08 to 0.46 mgL^{-1} and 0.14 to 0.20 mgL^{-1} respectively in the simulated leachates and are within the guideline limits for wastewater effluents set by the National Environmental Standards and Regulations Enforcement Agency [10], shown in Table 2.

Table 2: Average heavy metals concentration in simulated leachates

Sample	METALS (mgL^{-1})							
	Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
AD	0.53	0.52	72.27	0.50	0.08	3.60	1.71	0.13
MD	1.07	0.95	31.57	0.51	0.45	3.00	3.42	0.19
NESREA, 2007	< 1	< 1	5	0.5	< 1	< 1	< 1	20

Very high levels of manganese, nickel and cadmium were found in the simulated leachate that exceeded the guideline limits for wastewater effluents set by the National Environmental Standards and Regulations Enforcement Agency [10].Metallic compounds tend to degrade slowly, under some conditions, metals may, however, become rapidly mobilized [12 & 13]. The very high concentration of nickel in the simulated leachate indicates the possible disposal of batteries and nickel-containing scraps at these landfill sites.

The concentrations of lead range from 0.53 to 1.07 mgL^{-1}, Malali dumpsite had lead concentration above the guideline limits for wastewater effluents set by National Environmental Standards and Regulations Enforcement Agency [10]. The high concentration of lead in the simulated leachate could be due to the possible disposal of lead-based scraps or chemicals at the landfill sites [12 & 13].

Adsorption of heavy metal ions by various kinds of adsorbents has focused on the uptake of single metal ions, while in in leachates or wastewaters, the metals of interest are usually found with a number of other metals. The results of percentage adsorption of heavy metals from simulated solid waste leachate by Sawdust and Rice husk are presented the Tables 3:

Table 3: Percentage removal of heavy metals from simulated leachate.

DUMPSITE LEACHATE	ADSORBENT	% REMOVAL							
		Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
AD	RH	49.98	98.74	86.46	90.67	75.00	70.37	98.28	85.54
	SD	83.33	98.95	92.74	86.93	83.37	86.11	98.63	92.08
MD	RH	87.54	98.74	60.44	93.35	96.96	91.67	99.59	88.00
	SD	58.28	90.76	77.27	97.46	98.48	81.67	99.39	95.00

RH: RICE HUSK; SD: SAWDUST

For lead, sawdust is a better adsorbent compared to rice husk in the simulated leachates' investigated from one dumpsite, while rice husk showed better adsorption performance in the other dumpsite.

For the heavy metals copper, cobalt, cadmium and nickel, both adsorbents (sawdust and rice husk) were found to be suitable for the removal of these metals by more than 44% in all simulated leachates and up to 99% in one case. The binding mechanisms of heavy metals by biosorption could be explained by the physical and chemical interactions between cell wall ligands and adsorbatesand occurs predominantly by passive transport mechanisms and various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the cell wall of biosorbents can bind the heavy metals [14].

For chromium, iron and Manganese: Sawdust is a more suitable adsorbent for the removal of this metal than rice husk in all cases for the removal of the heavy metal in the simulated leachates. The major components of the polymeric material in sawdust are lignin, tannins or other phenolic compounds. From the nature of the material that are efficient in capturing heavy metal ions, it can be speculated that lignin, tannins or other phenolic compounds are the active ion exchange compounds and that active sites are the phenolic groups of those compounds [15].

The results of percentage adsorption of heavy metals from simulated solid waste leachate for composite adsorbent mix are presented the Tables 4:

Table 4: Percentage removal of heavy metals from simulated leachate

COMPOSITE MIX	Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
AIRPORT/LAGOS ROAD DUMPSITE								
CM1	86.06	99.21	98.76	99.84	97.41	77.85	99.91	79.43
CM2	49.10	99.18	98.84	99.88	97.17	82.04	99.44	84.30
CM3	78.66	99.75	98.86	99.90	91.13	86.22	99.89	83.07
MALALI DUMPSITE								
CM1	89.33	99.71	95.36	99.87	99.41	91.67	99.96	98.35
CM2	93.05	99.70	95.16	99.82	99.11	73.42	99.92	87.53
CM3	82.13	99.64	95.56	99.73	99.26	80.96	99.85	84.97

CM1 = COMPOSITE MIX 1: 25% RICE HUSK + 75% SAW DUST
CM2 = COMPOSITE MIX 2: 75% RICE HUSK + 25% SAW DUST
CM3 = COMPOSITE MIX 3: 50% RICE HUSK + 50% SAW DUST

Overall Composite mix 1 is a more suitable adsorbent compared to composite mix 2 and 3. Similarly Composite Mix 1 adsorbed more of the metals compared to Sawdust and Rice husk alone in the removal the metals investigated with the exception of iron and nickel in the simulated leachates, considering that Sawdust and Rice husk are complex materials withmany possible binding sites [15], a combination of both adsorbent may have enhanced its metal-adsorbent binding capacity.

Adsorption Isotherms For Composite Mix 1 :
From the mass balance the amount of adsorbed metal ions was then calculated to get the adsorption capacity, defined as:

$$q_t = \frac{(C_i - C_f)\, V}{m} \qquad (1)$$

Where, C_i and C_f are the initial and equilibrium or unadsorbed concentrations of metal ions in solution, q_t (mgg^{-1}) is the amount of adsorption per unit mass of adsorbent, V is the volume of adsorbate (L) and m is the amount of adsorbent (g) [16].

To quantify the adsorption capacity of the Composite Mix 1 for the removal heavy metal ions from solid waste leachate, the Langmuir and Freundlich models were used.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites [17]. It is represented by the following linearized equation:

$1/q_t = 1/q_e + (1/K_Lq_e)(1/C_e)$ (2)

q_e and K_L are Langmuir constants related to the adsorption capacity and energy of adsorption respectively. These values can be obtained from a plot of $1/q_t$ against $(1/C_e)$[17].

The Freundlich adsorption isotherm was also applied to the adsorption of metal ions from the simulated leachates. The Freundlich equation is represented as:

$q_t = K_FC_e^{1/n}$ (3)

Or

$Log\ q_t = Log\ K_F + 1/n\ Log\ C_e$(4)

From a plot of $Log\ q_t$ vs. $Log\ C_e$, the constant K_F and exponent 'n' can be determined [17].

In both isotherms C_e is the concentration of solute remaining in solution at equilibrium (mgL^{-1}), q_t is the amount of solute adsorbed per unit weight of solid adsorbent at equilibrium (mg/g).

Values of Langmuir and Freundlich parameters for each metal ion in the simulated leachates,and its respective correlation coefficient (R2) value are presented in Tables 5 and 6.

Table 5: Langmuir parameters

		METALS							
		Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
AD	K_L	60.71	1261.77	7.00	1.21×10^{-14}	107.58	85.36	675.53	64.56
	q_e	0.01	0.05	714.29	0.05	0.01	0.23	0.17	0.01
	R^2	0.82	0.76	0.89	1.00	0.69	0.97	0.89	0.79
MD	K_L	427.25	2636.28	244.29	754.95	334.33	76.29	104.27	24.46
	q_e	0.08	0.09	2.92	0.05	0.05	0.18	0.34	0.01
	R^2	0.93	0.79	0.98	0.70	0.84	0.92	0.87	0.94

Table 6: Freundlich parameters

		METALS							
		Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
AD	K_F	6.97×10^{-3}	0	7.14	0.05	4.51×10^{-3}	7.60	0.17	4.92×10^{-3}
	n	2.82	3.09×10^{-3}	270.27	6.02×10^{-12}	15.12	3.42	303.03	7.17
	R^2	0.90	6.24×10^{-5}	0.47	1.00	0.88	0.97	0.98	0.91
MD	K_F	0.04	0.09	3.07	0.05	0.04	0.02	0.04	0.01
	n	5.54	434.78	108.70	526.32	105.26	3.66	769.23	7.49
	R^2	0.98	0.92	0.86	0.76	0.96	0.98	0.93	0.94

Although both isotherms can be applied, the adsorption process of Composite Mix 1 overall is best fitted by the Freundlich adsorption isotherm based on their correlation coefficient R2. The Freundlich-type adsorption isotherm is an indication of surface heterogeneity of the adsorbent. This leads to the conclusion that the surface of composite mix 1 is made up of a mixture of heterogeneous adsorption patches that are similar to each other with respect to adsorption phenomenon [18].

Correlation values obtained from the plot of t/qt against t are shown in Table 7, though it is clear that metal ions compete with one another for the binding sites and considering that sawdust and rice husk are complex materials [15], a very good fitting (linear) graph was achieved between the experimental results confirming the second order kinetics of the adsorption.

Table 7: Correlation Coefficient (R^2) Values

LEACHATE	R^2							
	Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
AD	0.9987	1	0.9986	1	0.9911	0.9942	1	0.9974
MD	0.9983	1	0.9997	1	0.9999	0.9817	1	0.9838

The correlation coefficient (R2) values are close to or equal to1, this indicates that the pseudo-second-order model can be applied for the entire adsorption process for composite mix 1. Similar conclusion was also reported for the sorption of some heavy metal ions onto various adsorbent surfaces by some authors[19, 20, 21 & 22].

IV.   Conclution

1. The heavy metal concentration of   Lead, Nickel, Cadmium and Manganese in the leachates exceeds the guideline set by the NESREA, 2007.
2. Sawdust adsorbed more heavy metals than rice husk in the simulated leachates. Composite Mix 1 (25% rice husk + 75% sawdust) adsorbed more of the metals in the leachate than Composite Mix 2 (75% rice husk + 25% sawdust) and Composite Mix 3 (50% rice husk + 50% sawdust). The results suggests that the performance of Composite Mix 1 is better than either rice husk or sawdust alone in the removal of six out of the heavy metals studied.
3. The adsorption isotherm studies from the experimental data for composite mix 1 obtained showed that both Langmuir and Freundlich were applicable to the adsorption of heavy metals studied depending on the simulated leachate considered.
4. The experimental data for composite mix 1 were better described by pseudo-second order model as evident from correlation coefficients (R2 values) when the experimental data is regressed against a pseudo-second order equation.

The results showed that composite mix 1 (25% Rice Husk + 75% Sawdust) have been successfully used as an adsorbent for the removal of the heavy metal studied from dumpsite simulated leachates. Composite mix 1 is a good adsorbent for the efficient removal of the heavy metals from leachates containing heavy metal ions and is hence recommended for the removal of these metals in dumpsite leachates and other similar effluents.

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