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Sorption Behaviour of Composite mix of Agricultural Waste in the removal of Heavy Metals from Simulated Landfill Leachates

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Abstract: *Leachates from two dumpsites in Kaduna metropolis were simulated from decomposing solid waste soil samples. 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 leachates. The heavy metal concentration of lead (2.49 – 4.80 mgL^{-1}), nickel (1.40 – 1.80 mgL^{-1}), and manganese (22.78 – 58.77 mgL^{-1}) exceeded the guideline limits for wastewater effluents set by the National Environmental Standards and Regulation Enforcement Agency (NESREA, 2007). Sawdust is a more suitable adsorbent compared to rice husk in the removal of heavy metals from the simulated landfill leachates. 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 Freunlich models were applicable to the adsorption of the metals studied and the experimental data were better described by the pseudo-second order kinetic model.*

Keywords*: Adsorption, Heavy metals, Leachate and Agriculcural waste*

I. Introduction

Over the last four decades there has been increasing global concern over the public health impacts attributed to environmental pollution. Landfilling and or open dumping of wastes are very common methods of managing wastes in most third world countries[1].Depending on a city's level of waste management, such waste is usually dumped in an uncontrolled manner or simply burnt. Poor waste management poses a great challenge to the wellbeing of city residents; particularly those living near the dumpsites due to the potential of the waste to pollute water, land and air. The poor disposal and handling of waste thus leads to environmental degradation, destruction of the ecosystem and poses great risks to public health.

Unlined sanitary landfills have been reported to release large amounts of hazardous and deleterious chemicals including heavy metals to nearby ground water and to the air, via leachate and landfill gas respectively [1].

Some heavy metals such as lead (Pb); cadmium (Ca), manganese (Mn), copper (Cu)etc. are toxic and may be found in Landfill leachates.A wide variety of agricultural byproducts (or agricultural wastes) have been used for the removal of these metals from aqueous solutions by different investigators. The purpose of this work is to evaluate the use of Composite Mix of sawdust and rice husk for pollution controlof some heavy metals present in landfill leachates.

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 Gonin Gora (GD) at the outskirts of the metropolis and NEPA-Mando (ND) located within the metropolis shown in figure1.

III. 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 [2], kept in polythene bags and labeled, these were then transported to the laboratory where the samples were air-dried and sieved.

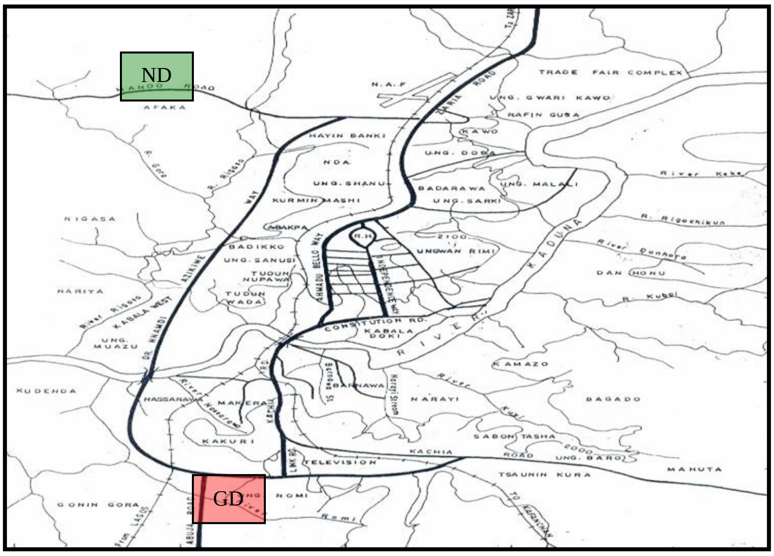

Fig. 1: Map Of Kaduna Metropolis

Key to dump sites:

ND **ND**: NEPA-Mando Dumpsite GD **GD**: Gonin Gora Dumpsite

IV. Adsorbent Collection And Preparation:

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 [3].

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 prepared according to the ratio stated above.

V. Leachate Simulation:

Leachate simulation experiment was carried out by a modified method of Alimba *et al*., 2006 [3], by weighing 700 grams of the decomposing solid waste soil samples into different 5-litreglass containers. Exactly 2.8 litres of distilled water (four times the sample weight) was then added to each container. 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^oC. The simulated leachates were then analyzed for heavy metals before the adsorption experiments.

VI. Batch Experiments

The batch experiments were carried out through the method of Ekop and Eddy, 2006[4] and Nemani*et al*., 2008 [3]. One gram of the adsorbent was weighed into a conical flask and 100 cm^3 of the simulated leachate added. The suspensions was agitated at 250-rpm agitation speed with a Stuart Mechanical Shaker at room temperature for 2 hours and for various contact time, ‘t’ (5, 10, 15, 20, 30, 45, and 60 minutes) respectively, the suspensions were then filtered into labelled 100 cm^3 plastic bottles through Whatman No. 540 filters paper to remove any suspended adsorbent and stored for elemental analysis.

VII. 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.

VIII. Results And Discution

Leachate quality varies widely depending on waste type and the waste age (Aik*et al*., 2010). 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 5.75 acidic to 8.72 moderately basic, the simulated leachate sample from NEPA-Mando (ND) dumpsite was outside the guideline limits set by the National Environmental Standards and Regulations Enforcement Agency[5] for wastewater effluents.

Table 1: Some Physicochemical Properties of Simulated Leachate

DUMPSITE	PHYSICOCHEMICAL PROPERTY		
	pH	CONDUCTIVITY (mScm^{-1})	TDS (gL^{-1})
GD	8.72 ± 0.22	2.24 ± 0.11	1.12 ± 0.03
ND	5.75 ± 0.22	0.72 ± 0.03	1.46 ± 0.05
NESREA, 2007	6 – 9	-	2.00

NESREA: National Environmental Standards and Enforcement Regulations Agency

Total dissolved solids (TDS) of the simulated leachate samples range from 1.12 gL^{-1} to 1.46 gL^{-1}. All the simulated leachates samples have values below the guideline limits of 2.00 gL^{-1} for wastewater effluents set by the National Environmental Standards and Regulations Enforcement Agency [5].

Conductivity of the simulated leachates samples range from 0.72 mScm^{-1} to 2.24 mScm^{-1} for NEPA-Mando and Gonin Gora dumpsites respectively. Although the National Environmental Standards and Regulations Enforcement Agency[5] do not have guideline limit for conductivity, the relatively high values of electrical conductivity indicate the possible presence of inorganic substances in the leachate samples.

Oygard*et al.*in 2006[6] observed that heavy metals leached from a landfill are usually found in the form of free cation, dissolved organic compound complex, particulate and colloid.The results of heavy metal concentration of the simulated leachates from decomposing solid waste samples from the four investigated dumpsites are presented in Table 2.

Table 2: Heavy Metals Concentration in Simulated Leachates

Sample	METALS (mgL^{-1})							
	Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
GD	2.4888	0.6496	22.7828	0.2708	0.1352	1.8000	0.0612	0.1668
ND	4.8000	0.6976	58.7676	0.3684	0.5956	1.4000	0.4640	0.4136
NESREA, 2007	< 1	< 1	5	0.5	< 1	< 1	< 1	20

The concentrations of copper, cobalt, chromium, cadmium and iron were within the guideline limit set for wastewater effluents by National Environmental Standards and Regulations Enforcement Agency.The heavy metal lead, manganese and nickel have concentrations above the NESREA guideline limit set for wastewater effluents.Metallic compounds tend to degrade slowly, under some conditions, metals may, however, become rapidly mobilized [7 & 8].

The result of adsorption of heavy metals by rice husk, sawdust and composite mix of both adsorbent are presented in Tables 3 and 4. For the simulated leachate from Gonin Gora dumpsite, sawdust adsorbed more of the heavy metals (Pb, Cu, Mn, Cr and Cd) compared to rice husk (Co, Ni and Fe), Similarly sawdust removed more of the metals (Pb, Mn, Co, Cr, and Fe) compared to rice husk (Cu, Ni and Cd) from the simulated leachate from NEPA-Mando dumpsite.

Table 3: Percentage Removal of Heavy Metals from Simulated Leachate.

DUMPSITE LEACHATE	ADSORBENT	% METAL							
		Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
GD	RH	85.71	98.31	85.47	86.72	60.00	80.56	44.26	86.83
	SD	87.50	99.49	98.96	84.50	85.19	72.22	77.05	85.63
ND	RH	93.52	97.99	65.22	86.96	91.95	75.00	98.49	94.20
	SD	96.29	89.97	79.43	97.55	96.48	42.86	98.00	95.17

RH: Rice Husk; SD: Sawdust

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 [9].

Table 4: Percentage removal of heavy metals from simulated leachate for composite Mix

	Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
GONIN GORA DUMPSITE								
CM1	95.92	99.60	95.57	99.74	98.96	68.26	96.89	97.00
CM2	89.10	99.33	97.09	99.74	96.89	61.98	93.46	81.06
CM3	87.51	99.51	95.98	99.74	96.15	72.45	93.30	74.10
NEPA-MANDO DUMPSITE								
CM1	98.84	99.68	97.21	99.89	99.10	37.64	99.61	91.10
CM2	98.27	99.57	95.80	91.67	99.62	64.58	99.38	95.99
CM3	98.15	99.66	96.20	91.67	99.29	75.35	98.20	97.20

CMI - Composite mix 1: 75% Sawdust + 25% Rice Husk
CM2 - Composite mix 2: 25% Sawdust + 75% Rice Husk
CM3 - Composite mix 3: 50% Sawdust + 50% Rice Husk

Composite Mix 1 adsorbed more of the metals compared to Composite Mix 2 and 3 overall, it also showed better performance in the removal of heavy metals compared to rice husk and sawdust alone.Sawdust and rice husk are complex materials and a combination of both adsorbent may have enhanced its metal-adsorbent binding capacity.

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)[10].

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[11]. It is represented by the following linearized equation:

$$1/q_t = 1/q_e + (1/K_L q_e)(1/C_e) \qquad (2)$$

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 ($1/C_e$) [11].

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

$$q_t = K_F C_e^{1/n} \qquad (3)$$

Or

$$\text{Log } q_t = \text{Log } K_F + 1/n \text{ Log } C_e \qquad (4)$$

From a plot of Log q_t vs. Log C_e, the constant K_F and exponent 'n' can be determined [11].
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 (R^2) value are presented in Tables 5 and 6.

Table 5: Langmuir Parameters

		METALS							
		Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
GD	K_L	1068.75	1569.86	281.29	4.42×10^{-14}	340.77	235.96	24.83	183.66
	q_e	0.21	0.07	2.09	0.03	0.01	0.12	0.01	0.02
	R^2	0.88	0.72	0.93	1.00	0.38	0.86	0.90	0.81
ND	K_L	726.74	2012.07	108.53	1190.48	1136.12	85.44	71.17	175.19
	q_e	0.43	0.07	5.42	0.04	0.06	0.07	0.05	0.04
	R^2	0.96	0.44	0.99	0.04	0.84	0.93	0.61	0.70

Table 6: Freundlich Parameters

		METALS							
		Pb	Cu	Mn	Co	Cr	Ni	Cd	Fe
GD	K_F	0.25	0.06	2.21	0.03	0.01	0.07	$2.58x10^{-3}$	0.01
	n	30.49	357.14	86.21	$1.75x10^{13}$	42.55	4.45	9.87	17.04
	R^2	0.15	0.02	0.56	1.00	0.90	0.97	0.97	0.53
ND	K_F	0.36	0.02	5.31	0.04	0.06	0.02	0.04	0.03
	n	16.81	250.00	24.21	312.50	232.56	2.24	140.84	21.74
	R^2	0.99	0.79	1.00	0.60	0.96	0.83	0.95	0.92

Table 7: Description of Isotherm Constants

ISOTHERM	CONSTANT	DESCRIPTION
LANGMUIR	K_L	Energy of adsorption (Lmg^{-1})
	q_e	Adsorption capacity (mgg^{-1})
FREUNDLICH	K_F	Maximum adsorption capacity (Lmg^{-1})
	n	Adsorption intensity

Gonin Gora dumpsite: for the heavy metals Pb, Cu, Mn and Fe Langmuir isotherm is most applicable while Freundlich best fit Cr, Ni and Cd. Both isotherms are applicable to the metal Co. Mixing of the adsorbent and wastewater (leachates) solution would be imperfect and the assumptions required by the Langmuir or Freundlich isotherms would less likely to be correct [12].

NEPA-Mando dumpsite: Freundlich isotherm is most applicable to all the metals except Nickel. The Freundlich-type adsorption isotherm is an indication of surface heterogeneity of the adsorbent while Langmuir-type isotherm hints toward surface homogeneity of the adsorbent. This leads to the conclusion that the surface of Composite Mix of rice husk and sawdust is made up of heterogeneous adsorption patches that are very much similar to each other with respect to adsorption phenomenon [13].

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 with many possible binding sites [9], a very good fitting (linear) graph was achieved between the experimental results confirming the second order kinetics of the adsorption.

TABLE 8: 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
GD	0.9963	1	0.9998	1	0.9994	0.9906	0.9968	0.9945
MD	0.9983	1	0.9997	1	0.9999	0.9817	1	0.9838

The correlation coefficient (R^2) values shown in Table 8 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, Augustine *et al*. in 2007 [14] and Velizar*et al*. in 2009 [15] reported similar conclusion for the sorption of some heavy metal ions onto various adsorbent surfaces.

IX. Conclusion

The heavy metal concentration of Lead, Nickel, and Manganese in the simulated leachates exceeds the guideline set by the National Environmental Standards and Regulation Enforcement Agency [5], and hence posses an environmental problem.

The use of sawdust as an adsorbent of heavy metals is more suitable than rice husk in the simulated leachates while Composite Mix 1 (25% rice husk + 75% sawdust) adsorbed more of the metalsoverall compared to Composite Mix 2 (75% rice husk + 25% sawdust) and Composite Mix 3 (50% rice husk + 50% sawdust). The performance of composite mix 1 is better than either rice husk or sawdust alone.

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 and the experimental data for Composite Mix 1 were better described by pseudo-second order model as evident from correlation coefficients (R^2 values) when the experimental data is regressed against a pseudo-second order equation.

Composite mix 1 is a good adsorbent for the efficient removal of the heavy metals from landfill leachates containing heavy metal ions and is hence recommended for the removal of these metals in dumpsite leachates and similar wastewater effluents.

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