Uptake of Zn, Pb, Cu and Fe Ions from Spent and Unspent Engine Oil Using Termite Soil

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Abstract

Removal of Zn, Pb, Cu and Fe ions from unspent and spent engine oil was studied using Termite soil. Process parameters such as contact time and adsorbent dosage were varied. Values from contact time were used for predicting kinetics equation of their uptake. At optimum time of 40 minutes, percentage adsorption was of the order Fe>Zn>Cu>Pb for both spent and unspent engine oil. Kinetics equation such as Elovich, Intra-particle, Pseudo-first order and Pseudo-second order were tested. Results obtained shows that their sequestering pattern fit into the pseudo-second order kinetics. Initial reaction rates, h (mg/g.min) and α (mg. $g^{-1}min^{-1}$) for all metal ions obtained from Pseudo-second order and Elovich kinetic models followed the trends Zn>Fe>Cu>Pb and Zn>Fe>Pb>Cu respectively in spent engine oil while for unspent engine oil, the trend was Fe>Zn>Cu>Pb for h (mg/g.min) and Zn>Fe>Pb>Cu for α (mg. $g^{-1}min^{-1}$). Electrostatic attraction existing on the surface of the adsorbent assisted in the high initial reaction of Zn and Fe ions, implying good affinity of the ions for the adsorbent. Desorption constant β (g/mg) was of the trend Cu>Pb>Fe>Zn and Cu>Pb>Zn>Fe for spent and unspent engine oils respectively. Intra-particle diffusion constant k_{id} ($mgg^{-1}min^{-1/2}$) followed a similar pattern, revealing strong binding between Zn and termite soil than any of the metal ion. This pilot research has been able to suggest a kinetic process for uptake of the studied ions from spent and unspent engine oil.

Keywords: spent and unspent engine oil, termite soil, metal uptake, adsorption kinetics

1. Introduction

Spent motor oil is an alarming environmental pollutant and is usually obtained after servicing and subsequent draining from automobile and generator engines by auto-repairers (Sharifi et al., 2007). Some major pollutants found in spent lubricating oil include polynuclear aromatic hydrocarbons (PAHs) and high levels of heavy metals. Considerable quantities of heavy metals, such as Pb, Zn, Cu, Cr, Ni, and Cd, are contained in used crankcase oil (Vwioko and Fashemi, 2005). Improper disposal of spent engine oil leads to a buildup of essential inorganic nutrients such as phosphorus, calcium, and magnesium, and trace amounts of lead, zinc, iron, copper and cobalt. These elements if in excess accumulate in plant tissues. Although some heavy metals at low concentrations are essential micro nutrients for plants, at high concentrations they could cause high metabolic disorder and growth inhibition for most plant species. Spent engine oils are particularly dangerous to the environment due to their contamination with products of thermal decomposition and mechanical impurities. These pollutants become hardly biodegradable and have carcinogenic properties (Grzegorz et al., 2015).

Contaminations of soil with engine oil are rampant in the Nigerian environment and have adversely affected seasonal crops such as maize (Kelechi et al., 2012; Agbogidi et al., 2007).

In Nigeria, the Government has not been able to monitor or control the discharge of used oils and grease from the numerous auto- repair workshops littered over the country because they have proven to be very difficult to regulate their activities by virtue of their small size (Ahamefule, 2013).

Several adsorbents such as agricultural waste have been investigated for sequestering of heavy metals from various waste matrices. In recent times, termites soils have been investigated and reported to have high porosity and water infiltration due to buildup of have galleries (Schaefer, 2001; Dangerfield et al., 1998) which makes it a suitable

adsorbent for metal removal (Agbozu and Bassey, 2016). Also, pH of termite soil tends to be higher than that of adjacent soils thereby causing an increase in adsorption sites (Holt *et al*., 1998).

Adsorption kinetics is important in the evaluation of the performance of a given adsorbent and underlying mechanisms of sorption. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information. Generally speaking, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems (Dabrowski, 2001). Adsorption kinetics is determined by the following stages: 1) diffusion of molecules from the bulk phase towards the interface space commonly called external diffusion; 2) diffusion of molecules inside the pores internal diffusion; 3) Adsorption-desorption elementary processes (Sharma, 1990).

1.1 Lagergren Pseudo-first Order Model

The pseudo first-order kinetic model (Lagergren's equation) describes adsorption in solid–liquid systems based on the sorption capacity of solids. It assumes that one metal ion (adsorbate) is adsorbed onto one sorption site on the adsorbent surface:

1.2 Pseudo-second Order Model

The pseudo second-order rate expression has been applied for analyzing chemisorption kinetics from liquid solutions. The model assumes that one metal ion (adsorbate) is sorbed onto two sorption sites on the adsorbent surface:

1.3 Elovich Model

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate–adsorbent relationship.

In order to avert the problem of soil pollution caused by used engine oil, there is need to study the adsorption kinetics of termite soil for the removal of heavy metals (Pb, Fe, Zn, and Cu) from spent and unspent engine oil through adsorption process.

2. Materials and Methods

2.1 Sampling

Termite soil was collected from Ugbomro Community in Uwvie Local Government Area of Delta State, Nigeria at Latitude N 05° 34' 09.8" and Longitude E 005° 50' 23.0".

2.2 Pretreatment

The termite soil was air dried at room temperature for 72 hours and crushed in a mortar. The sample was pretreated to remove non clay material such as carbonate and quartz minerals. A 2M Hydrochloric acid (HCl) was added to 0.6mm particle sized adsorbent to remove heavy metals present in the adsorbent and improve the sorption property of the absorbent. The mixture was stirred for 1 hour and allowed to remain in a plastic for 24hours and then thoroughly washed with distilled water and air dried for 2days. Virgin (unspent engine) oil with Society of Automotive Engineers (SAE) Grade of 20W-50 was used in a generator running at 6 hours daily for one week. Residual engine oil was collected after 42 hours of usage in the generator and labeled as spent engine oil.

2.3 Initial Concentration of Heavy Metals in Adsorbent and Adsorbate

A 0.5g of the termite soil was weighed into a 100ml beaker, and then 20ml of an aqua regia mixture (15ml conc. HCl, 5ml conc. HNO_3 in the ratio of 3:1) was added to the soil sample in the beaker. The sample was then digested using a block digester under fume hood for 15 minutes. The solution was allowed to cool, and then filtered into a 100 ml Pyrex and immediately transferred into 120ml plastic container. Concentrations of heavy metals were determined using atomic absorption spectrophotometer (spectral 220 FX). similarly, 5ml of the spent engine oil sample was measured, and added to a mixture of 20ml HNO_3 and HCl (5ml HCl +15ml HNO_3) (Yong *et al*., 2016). Results from the analysis were used as initial concentration of metal ions. Same process was used for digestion of unspent engine oil.

2.4 Adsorption Techniques

A glass separating funnel was fitted with cotton wool and held firmly in a vertical position with the aid of a retort stand. Atmospheric pressure helped to push the sample through the adsorbent. Adsorption process was carried out at room temperature. Process parameters such as contact time and adsorbent dosage were varied.
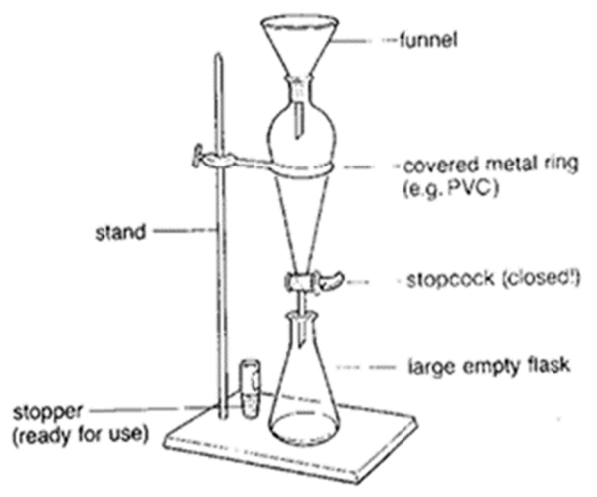
Figure 1. Experimental setup during adsorption process

2.5 Contact Time

A 0.5g of termite soil with mesh size 0.6mm was packed in a column and 5ml of spent engine oil was introduced and allowed to remain in the column for 10, 20, 30 and 40 minutes respectively before elution as shown in Figure 1. After each contact time, the filtrate obtained was digested and the digest was stored in a polyethylene container for metal analysis using the Atomic Adsorption Spectrophotometer. Similar process was used for unspent engine oil.

2.6 Adsorbent Dosage

Adsorbent dosage of 0.1, 0.2, 0.3, 0.4, and 0.5g of 0.6mm mesh size were investigated. The adsorbent was packed in a column; 5ml of spent engine oil was introduced and allowed to remain in the packed column for the studied optimum contact time of 40mins. Thereafter, the filtrate was digested and the digest stored in a polyethylene container for metal determination. Similar process was used for unspent engine oil

2.7 Infra-red Spectrometric Analysis of Termite Soil

In other to determine functional groups present in the adsorbent, 100 mg of the termite soil was dissolved in 2 ml of hexane. Two drops of the mixture was placed on a clean salt (NaCl) plate and the solvent was allowed to evaporate, leaving a cast film of the adsorbent. The cast film of the adsorbent was transferred to the PLC-11M Prism Cell. The resulting sample was scanned using infra-red spectrophotometer M500.

2.8 Data Analysis

The following kinetics equations were explored to determine the movement of various metal ions to the surface of the adsorbent.

Kinetic equations

$$\text{Adsorption capacity } q_e \text{ (mg/g)} = \frac{(C_0 - Ce)v}{m} \tag{1}$$

$$\text{Pseudo first order kinetics Log } (q_e - q_t) = \text{Log } q_e - \frac{k_1}{2.303} \tag{2}$$

$$\text{Pseudo second order kinetics } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

$$\text{Intra-particle diffusion } q_e = k_{\sqrt{t}} + C \tag{4}$$

$$\text{Elovich } q_e = \left(\frac{1}{\beta}\right) \text{In } (\alpha_\beta) + \frac{1}{\beta}\text{Int} \tag{5}$$

Where

M is the mass of adsorbent in gram,

C_0 and C_e are initial and final concentration of metal ions,

V is the volume of solution in litres and

q_t is the quantity of metal ions adsorbed at any particular time (mg/g).

β (g/mg) is desorption constant,

α (mg. g^{-1}min^{-1}) is the initial reaction rate from Elovich equation
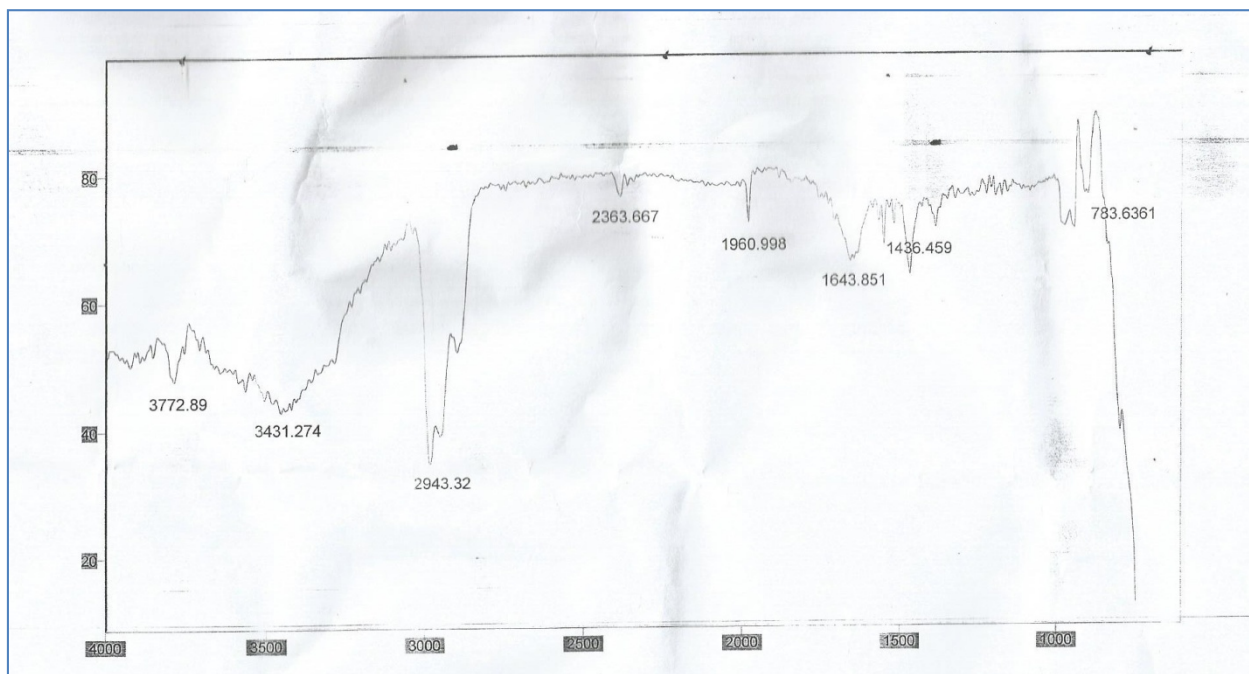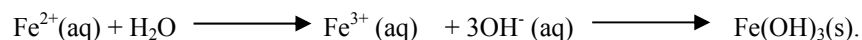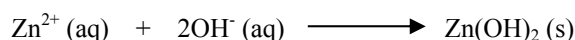
3. Result and Discussion

Figure 2. FTIR spectra in the 4000–400 cm^{-1} wave number range for termite soil

From Figure 1.0 the main bands appearing in that spectrum were due to stretching vibrations of OH groups in the range from 3750 –3000 cm^{-1}, which are overlapped to the stretching vibration of N-H; and C–H bond in –CH$_2$ (2943 cm^{-1}). Bending vibrations of methyl groups occurred at 1436 cm^{-1}, (Mano *et al*., 2003).Absorption in the range of 1643–1436 cm^{-1} was related to the vibrations of carbonyl bonds (C=O) of the amide group CONHR (secondary amide, 1643 cm^{-1}) (Marchessault *et al*., 2006).On the basis of interaction with functional group, hydroxide ions present in the adsorbent provide sites for chemisorptions of heavy metals. Surface reaction includes;

$$Zn^{2+} (aq) \quad + \quad 2OH^{-} (aq) \quad \longrightarrow \quad Zn(OH)_2 (s)$$

$$Fe^{2+}(aq) + H_2O \quad \longrightarrow \quad Fe^{3+} (aq) \quad + 3OH^{-} (aq) \quad \longrightarrow \quad Fe(OH)_3(s).$$

Similar reaction of Cu and Pb ions give product of their hydroxides. The ease at which this bond would be destroyed by water molecules is dependent on their enthalpies of hydration. The hydration energy for the +2 oxidation states of the studied metal ions are -1946 kJ/mol for Fe (II), -1480kJ/mol for Pb (II), -2046kJ/mol for Zn (II) and -2100kJ/mol for Cu (II) respectively. According to Ayuba and Khuzaifa (2014) stronger enthalpy of hydration leads to better adsorption and reduces the tendency for desorption. Therefore Zn and Cu ions would held strongly on the adsorbent with less ease of leaching away.

Table 1. Initial concentration (mg/l) of metal ions in spent and unspent engine oil

S/N	Metal	Spent engine oil	Unspent engine oil
1	Cu	4.94±0.5289	4.10±0.1405
2	Zn	226.35±8.8114	210.03±7.2351
3	Pb	10.38±0.5876	5.95±0.5896
4	Fe	38.70±3.3560	32.17±1.4351

Table 2. Concentration (mg/l) of metal ions in spent and unspent engine oil after adsorption

Contact time	Spent engine oil					unspent engine oil		
	Cu	Zn	Pb	Fe	Cu	Zn	Pb	Fe
10	4.45	162.07	10.02	34.98	3.82	142.19	5.85	23.57
20	4.00	124.94	9.82	26.00	3.14	132.38	5.64	12.57
30	3.98	115.66	9.60	22.52	2.94	115.51	5.56	10.73
40	3.50	85.33	9.00	12.69	2.66	114.09	5.52	9.29

Table 3. Concentration (mg/l) of metal ions in 0.5g adsorbent

Contact time	Spent engine oil				unspent engine oil			
	Cu	Zn	Pb	Fe	Cu	Zn	Pb	Fe
10	0.49	64.28	0.36	3.72	0.29	67.84	0.10	8.60
20	0.94	101.41	0.56	12.70	0.96	77.65	0.31	19.60
30	0.96	110.69	0.58	16.18	1.16	94.52	0.39	21.44
40	1.44	141.02	1.38	26.01	1.44	95.94	0.43	22.88

Table 4. Concentration (mg/l) of metal ions adsorbed during variation of adsorbent dosage at optimum time of 40 min

Dosage (g)	Spent engine oil				unspent engine oil			
	Cu	Zn	Pb	Fe	Cu	Zn	Pb	Fe
0.1	0.32	50.25	0.01	1.45	0.1	45.01	0.02	5.46
0.2	0.38	62.07	0.23	8.27	0.25	47.77	0.15	8.98
0.3	0.38	61.25	0.28	10.55	0.88	46.89	0.26	15.32
0.4	0.40	70.45	0.72	22.06	0.92	72.08	0.41	16.55

From Table 1, the order of heavy metals in both used and unused engine oil is Zn>Fe>Pb>Cu. The high concentration of zinc obtained may be due to the presence of additives such as Zinc diaryl or dialkyl dithiophosphates; zinc dithiophosphate, and other organometallic compounds found in engine oil which contains heavy metals (Masabumi *et al.*, 2008; Rizvi, 2009). The increase in the content of zinc in spent oils in comparison with unspent oil may be the result of the presence of wearing products. Its presence in used oils is mainly connected with bearing wear (Nwosu *et al.*, 2008). Copper in used engine oils comes mainly from the wearing products of the bearings, rings, and valve guides; in smaller quantities it is introduced in the form of additives (Palkendo *et al.*, 2014). Iron is the most typical engine wear product present in engine oil. Therefore, its concentration in spent oil mainly depends on lubricating conditions inside the engine. Njue *et al.* (1999) reported values of 20-788, 9-1550 and 6.5-170 in mg/l for Pb, Fe and Cu in spent engine oil collected from Nairobi central district in Kenyan.

From Table 2 the order removal of various metal ions using termite soil is as follows: for spent engine oil at 10 minutes Zn > Cu>Fe> Pb, 20 and 30 minutes Zn>Fe>Cu>Pb and 40 minutes Fe > Zn> Cu>Pb for unspent engine oil at10 minutes Zn>Fe>Cu>Pb, 20 to 40 minute Fe>Zn>Cu>Pb. An increase in adsorbent dose resulted to more uptake of metal ions as seen in Table 4. This is due to more porous adsorption sites.
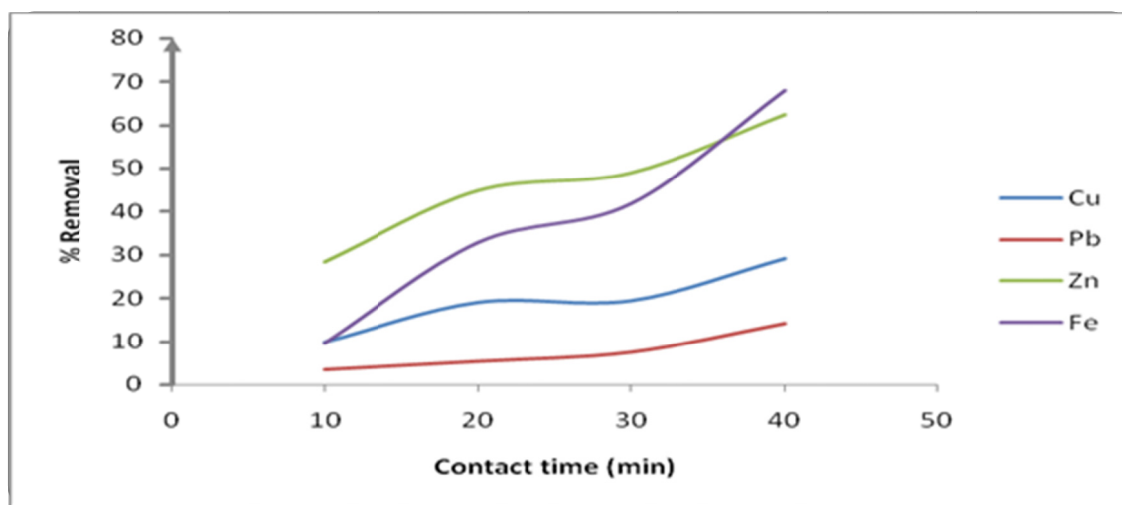

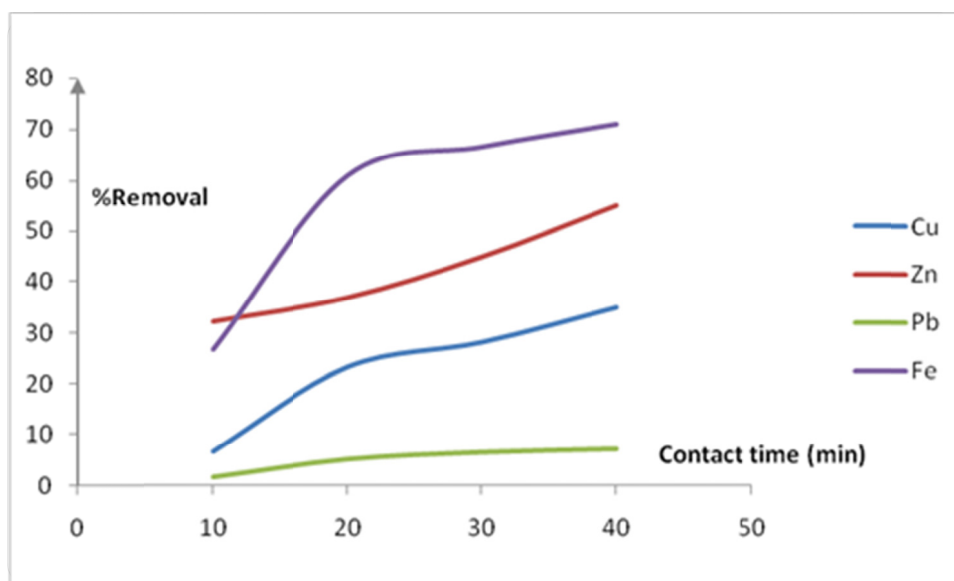Figure 3. Percentage removal of metal ions from spent engine oil

Figure 4. Percentage removal of metal ions from unspent engine oil

Percentage removal of studied metal ions as shown in Fig 3 and 4 increases with increase in contact time was also increased. This occurred as a result of availability of adsorption sites in the adsorbent.

Table 5. Kinetics parameters for spent engine oil

Pseudo first order kinetics				
Parameters	**Zn**	**Pb**	**Cu**	**Fe**
Q_t (mg/g)	1.5922	1.0234	1.4421	1.4928
Q_e (mg/g)	0.0141	0.0146	0.0144	0.2630
k_1(min^{-1})	0.0415	0.2349	0.1658	0.0737
R^2	0.967	0.771	0.708	0.876
Pseudo second order kinetics				
Q_t (mg/g)	0.0285	0.02430	0.0285	0.2615
Q_e (mg/g)	0.0141	0.0146	0.0144	0.2630
k_2 (g/mgmin)	0.0188	0.8468	0.7387	0.1535
h (mg/g.min)	0.08921	0.000313	0.000514	0.00366
R^2	0.983	0.905	0.982	0.900
Intra-particle diffusion				
C (mg/g)	-0.062	-0.007	-0.004	-0.179
k_{id} (mgg^{-1}min$^{-1/2}$)	0.227	0.003	0.002	0.067
R^2	0.964	0.841	0.912	0.958
Elovich				
α (mg/gmin)	0.1779	0.0011	0.00054	0.01775
β (g/mg)	1.9493	142.8571	333.333	6.71141
R^2	0.956	0.772	0.915	0.931

Q_e (mg/g); experimental adsorption capacity

Q_t (mg/g); theoretical adsorption capacity

Table 6. Kinetics parameters for unspent engine oil

Parameters	Zn	Pb	Cu	Fe
Pseudo first order kinetics				
Q_t(mg/g)	2.8445	1.5031	2.0328	3.1477
Q_e (mg/g)	0.1520	0.0323	0.0144	0.2288
K_1((min^{-1})	0.1359	0.1543	0.1842	0.1404
R^2	0.963	0.733	0.797	0.969
Pseudo second order kinetics				
Q_t (mg/g)	0.2873	0.0433	0.0215	0.4115
Q_e (mg/g)	0.1520	0.0323	0.0144	0.2288
K_2(g/mgmin)	0.0188	0.8468	0.7387	0.1535
h(mg/g.min)	0.0031	0.0027	0.0003	0.0138
R^2	0.982	0.927	0.945	0.964
Intra-particle diffusion				
C(mg/g)	0.0071	0.004	0.007	0.005
K_{id} (mgg^{-1}min$^{-1(1/2)}$)	0.037	0.002	0.003	0.004
R^2	0.941	0.936	0.963	0.952
Elovich				
α(mg. g^{-1}min^{-1}).	0.5354	0.00126	0.001227	0.1724
β (g.mg^{-1})	11.764	111.11	125.00	9.708
R^2	0.979	0.878	0.986	0.921

Q_e (mg/g); experimental adsorption capacity

Q_t (mg/g); theoretical adsorption capacity

Table 5 and 6 gives various parameters for Pseudo-first, pseudo-second, intra-particle and elovich parameters used in describing the factors influencing the movement of metal ions onto available adsorption sites on the adsorbent. It is observed that correlation coefficient for pseudo-first order kinetics is larger compared to other kinetics model, and had theoretical adsorption capacity close to the experimental value. Hence describes the pattern of movement of metal ions to the surface of the adsorbent. Also R^2 for spent and unspent engine are 0.983, 0.905, 0.982, 0.900 and 0.982, 0.927, 0.945, 0.964 respectively is greater compared to other kinetics models.

Graph of $\frac{t}{q_t}$ against t was used in determining initial reaction rate h(mg/g.min**)** as described by pseudo-second order

kinetics. Also plot q_t against Int gave elovich parameter α for initial reaction rate determination. Values obtained shows that Zn and Fe had fast uptake compared to Cu and Pb. The theoretical adsorption capacity also reveals the availability of Cu and Zn ions on the adsorbent surface. Possibly Pb and Cu ions tends to desorp away from the adsorbent upon getting to the surface as evidence from their high desorption constant as seen in the Tables 5 and 6, desorption constant is of the order Cu>Pb>Zn>Fe for spent engine oil Table 5.0 and Pb>Cu>Zn>Fe for unspent engine oil Table 6.0. Values obtained for pseudo-second order kinetics have less difference between theoretical (Q_t) and experimental adsorption (Q_e) capacity

Plot of q_t against √t were used in obtaining intra-diffusion parameters. Intercept C (mg/g) obtained from Tables 5 and 6 are negligible, implying insignificant restriction of boundary layer of the adsorbent for the uptake of the ions. According to Imaga and Abia (2015), for uptake of ions in a heterogeneous system to be best described by intra particle diffusivity the boundary layer C (mg/g) should be equal to zero. Values of boundary layer for the adsorbent during uptake of metal ions were not equal to zero. The observed values shows that the mode of transport is affected by more than one process such as surface adsorption, chemisorptions, ion exchange, precipitation and intra-particle diffusion are occurring concurrently (Igwe *et al*., 2005). Intra-particle diffusion constant (k_{id}) is of the order Zn>Fe>Pb>Cu. This reveals the affinity of the adsorbent (termite soil) with various metal ions. According to Itodo *et al*. (2010) higher values of k_{id} illustrate an enhancement rate of adsorption, which is related to improve bonding between adsorbate and adsorbent particles. Hence Zn ions formed strong bond with the adsorbent compared to other metal ions. Desorption constant 'beta' obtained shows that Zn ions has less potential to be leached from the pores of the adsorbent.

4. Conclusion

Result obtained reveals an increase in concentration of metals in engine oil after usage. This might be attributed to wear and tear of engine parts. However, there was a decrease in their concentration after adsorption. The level of uptake followed the order Fe>Zn>Cu>Pb. Several kinetics models were tested but pseudo-second order kinetics was the best for predicting the kinetics for uptake of the studied metal ions.`.

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