

DEVELOPMENT OF AN ECO-FRIENDLY TREATMENT METHOD FOR E-WASTE

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Abstract

E-Waste, the wastes arising from discarded electronic components, is one of the fastest growing waste streams which contain a number of hazardous substances. It is a complex mixture of toxic metals and polymers which, if disposed without proper treatment, can have major adverse impacts on the environment. The toxic metals can leach out and cause ecological and public health impacts.

In the present study, an environment friendly method has been developed, which allows the recovery of the toxic metals copper (Cu), Lead (Pb) and Zinc (Zn) from printed circuit boards (PCB). In this process, the metals were extracted from the finely ground and sieved PCB wastes by a sequential extraction process using 2N Hydrochloric acid. Stage wise extraction followed by pH adjustment under different conditions was able to selectively enrich Pb from other metals. From a screening of natural waste materials, alkali treated palm leaf powder was selected as a biosorbent to remove the metals from the acid extract. Complete removal of Pb and a high removal (82%) of Cu were observed at a biosorbent dose of 100 g/l. Both Freundlich and Langmuir isotherms fitted the batch adsorption data well.

Keywords: E waste, Toxic metals, Extraction, Biosorption, Isotherms

1. Introduction

Electronic waste is the term used to describe old, end of life or discarded appliances of modern electronic products. It includes computers, consumer electronics etc which have been disposed off by their users. The use of electronic devices has proliferated in recent decades, and proportionately, the quantity of electronic devices, such as PCs, mobile telephones and entertainment electronics that are disposed of, is growing rapidly throughout the world. The useful life of electronic items is relatively short, and decreasing as a result of rapid changes in technology, equipment features and capabilities. This creates a large waste stream of obsolete electronic equipment. Electronic waste is of concern largely due to the toxicity and carcinogenicity of some of its substances if processed improperly. E-waste contains many hazardous substances which are extremely dangerous to human health and environment, and therefore disposal requires special treatment to prevent the leakage and dissipation of the toxics to the environment. At the same time, it is a rich source of metals such as gold, silver and copper which can be recovered and brought back into the production cycle.

The significant component of E-waste is the printed circuit boards, which acts as a base and provides electrical connections to the mounted components. PCB contains heavy metals and precious metals (up to 40% by weight), polymers (30% by weight) and ceramics (30% by weight) (Ogunniyi et.al. 2009) From the point of material composition, e-waste can be defined as a mixture of various metals, particularly copper, aluminium and steel, attached to, covered with, or mixed with various types of plastics and ceramics. From the point of material composition, e-waste can be defined as a mixture of various metals, particularly copper, aluminium and steel, attached to, covered with, or mixed with various types of plastics and ceramics.

Toxic substances in electronic waste may include lead, mercury and cadmium. Carcinogenic substances in electronic waste may include polychlorinated biphenyls (PCBs). Many of the plastics used in electronic equipment contain flame retardants. There are generally halogen added plastic resins which are difficult to recycle. The flame retardants leach in to the soil and there are reports of recorded levels 93 times higher than soil without contact with electronic waste (Leung et al., 2003)

Even now the e-wastes generally are often disposed along with municipal solid wastes either in landfills/dumps or in incinerators. The environmental risk from landfilling can not be neglected because of leaching behaviour of metals. Landfills are also prone to uncontrolled fires, which can release toxic fumes. During incineration, the polymeric products can be a potential source of dioxins and the gaseous emissions may carry metals like cadmium, lead and mercury. The incinerator ash may also contain toxic heavy metals making it a hazardous waste. The present

work was aimed at developing an eco friendly method for the safe treatment and disposal of e wastes.

2. Materials and Methods

2.1 Chemicals : The chemicals used in the study were hydrochloric acid (HCl), sodium hydroxide (NaOH), cupric sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and lead nitrate ($\text{Pb}(\text{NO}_3)_2$). All reagents were of analytical grade and were obtained from SISCO Research Laboratory Private Limited (Mumbai, India).

2.2. Adsorbent: Biosorption of metals was studied with dried palm leaves (*Borassus flabellifer*), collected from IIT Madras Campus.

2.3 Waste PCB scraps: The PCBs used for study were taken from discarded electronic equipments available in IIT, Madras.

2.4 Metal analysis: Metal concentrations in the samples were analysed using an Atomic Absorption Spectrophotometer (Perkin Elmer Instruments, USA, model A Analyst 700)

2.5. Metal Extraction: Extraction with HCl was conducted to recover the metals available in the PCBs. The extraction conditions were optimized by changing the parameters (temperature, normality of HCl and time) of extraction. Batch extraction was carried out by mixing 25 ml of 2N HCl with one gram of solid sample in 100 ml conical flask and shaking at 120 rpm in a rotary shaker. Extract samples were taken at intervals $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, 6, 12 and 24 hours and were analysed for Cu, Pb and Zn using AAS.

2.6. Sequential Extraction : To improve efficiency of extraction of metals, sequential extractions, in two and three stages, were conducted at 50°C for 12 hours by taking sample from both coarse and fine fractions. In both two stages and three stages sequential extractions, the total quantity of solvent used was the same as that used in single stage extraction. To conduct two stages sequential extraction, 25 ml 2 N HCl was added to 2 g sample taken in a conical flask (stage 1), extract was removed after shaking for 6 hours and leaching was continued by adding 25 ml of fresh 2N HCl to the solid left over (stage 2). Both the extracts, from first and second stage, were mixed and analysed for heavy metals using AAS.

To conduct three stages sequential extraction, 17 ml 2 N HCl was added in each of the three stages. Initially, 17 ml HCl was added to 2g sample taken in a conical flask and was shaken for 6 hours (stage 1) at 50°C . The extract was removed and leaching was continued by adding fresh 17 ml HCl to the left over solid at the same temperature for 4 hours (stage 2). The extract obtained from second stage was replaced by fresh 17 ml HCl and was shaken for 2 hours. All the three extracts obtained from three stages were mixed and analysed for metals, Cu, Pb and Zn.

2.7 Preparation of adsorbents : The adsorbent was prepared by powdering dried palm leaves (*Borassus flabellifer*). The powdered adsorbent was sieved and the fraction having size <600 microns and >420 microns was selected for adsorption. This fraction was washed with water and dried. About 20 ml of 0.5 N NaOH was added to 2 g of palm leaf powder and gently heated for 20 minutes after boiling started. After cooling the adsorbent was washed with water to remove excess alkali and dried.

2.8 Adsorption of metals from extract using alkali treated palm leaf powder: 100 ml of extract was taken and adjusted the pH to 4. Adsorption equilibrium studies were conducted by varying the adsorbent doses. Three different adsorbent doses (50, 75 and 100 g/l) were used and adsorption was conducted for 10 hours at room temperature. Samples were collected at intervals of every 15 minutes for the first hour followed by hourly intervals up to 6 hours and then after 10 hours and analysed for residual concentrations of Cu, Pb and Zn using AAS. The percentage removal of the metals of interest was estimated from initial and residual metal concentrations.

3. Results and Discussion

Size reduction of PCB scraps was done to liberate metals from polymer and to increase the efficiency of extraction of metals by improving the metal – acid contact. This was done using a hammer mill after manual cutting of PCB scraps in to small pieces. The total quantity of metals present in the sample, which was obtained by acid digestion (assuming complete recovery is possible with acid digestion), is given in Table 1. The quantity of metals present in PCB scraps, obtained by acid digestion is matching with the data available in literature [1].

Table 1 : Total availability of metals in fine and coarse fractions, as obtained by acid digestion

Sample	mg of metal present per g sample		
	Cu	Pb	Zn
Fine	120	18	3.3
Coarse	158	50	17

3.1 Extraction at room temperature

A general trend in the extraction of metals from PCB scraps were obtained by conducting extraction using 2N HCl at room temperature (28°C). The variation in the amount of Cu, Pb and Zn extracted (in mg metal/g sample) with respect to time at room temperature is shown in Figures 1,2 and 3 respectively. For fine fraction, the extraction of Cu was significant after 2 hrs of extraction and was found to reach equilibrium as time progressed. There was not much increase after 12 hrs of extraction. But in the case of coarse fraction, the extraction was not much initially and after 6 hrs it started increasing. Equilibrium was not reached till 24 hrs of extraction.

Cu is present in PCB as thin film (coating) and hence the metal - polymer contact area is more. In fine fraction, due to small particle size, the degree of physical separation of metal from polymer is more, whereas in coarse fraction the metal is still combined with polymer. Better metal – polymer separation can be achieved by reducing the particle size. Hence extraction of Cu from fine fraction was faster than that from coarse fraction. The initial flat portion of the curve showing no significant extraction in the initial 2 hours, may be due to the incomplete liberation of the metal from polymer.

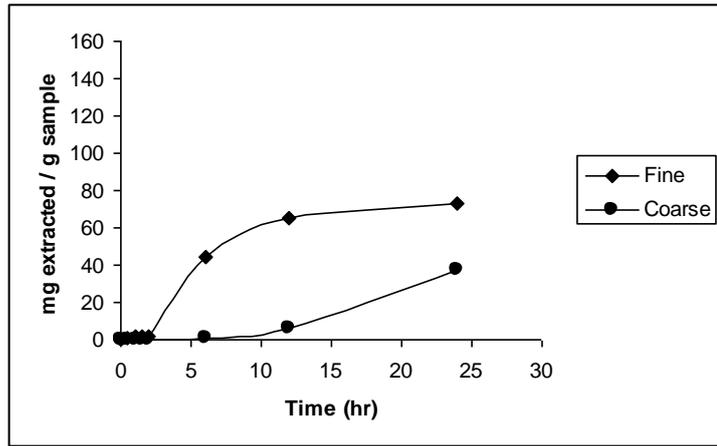


Fig. 1 Variation in the extraction of Cu with time of extraction for fine and coarse fractions at 28⁰C

Increase in extraction of Pb with respect to time (Fig. 2) was significant during the initial period of extraction itself. The extraction was almost complete within 1.5 hours of extraction and after that there was no significant increase in extraction of Pb. Unlike for Cu, extraction of Pb reached equilibrium in less than 24 hours of extraction. This is because Pb in PCB is present in solders and is not coated with polymer. So the degree of separation between metal and polymer is not highly dependent on particle size.

The extraction of Zn from fines (Fig. 3) was better initially compared to that from coarse but remained relatively low after 6 hours. But for coarse fraction, the increase in extraction was rapid after 6 hrs of extraction, though initially it was negligible.

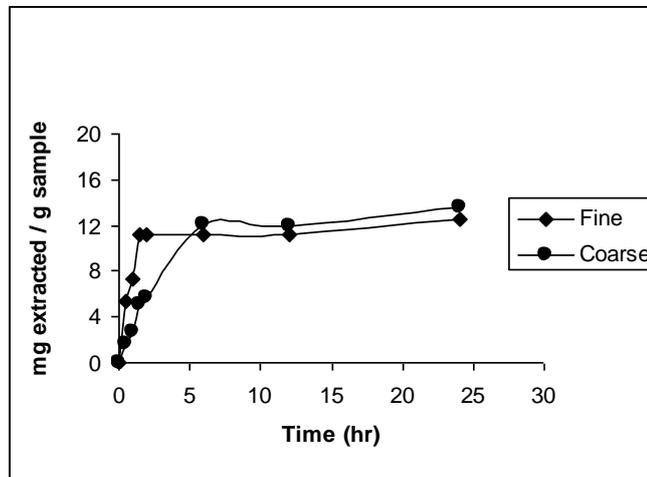


Fig. 2 Variation in the extraction of Pb with time of extraction for fine and coarse fractions at 28⁰C

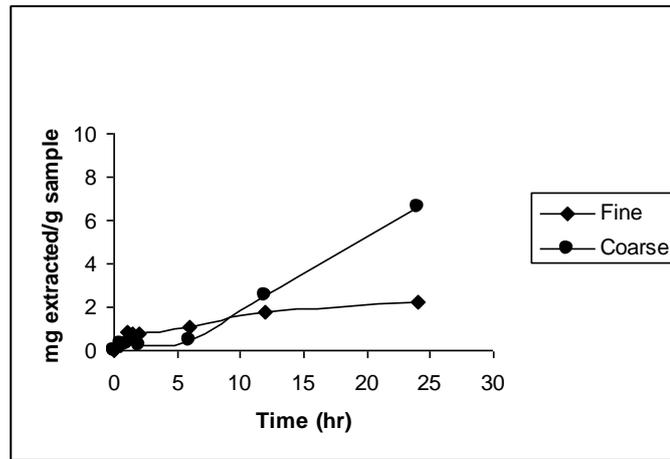


Fig. 3 Variation in the extraction of Zn with time of extraction for fine and coarse fractions at 28⁰C

This may be due to the presence of Zn in PCB in both thick (solder) and thin (coating) forms. So some amount of Zn (from solder) is free to enter the solution and some still bonded with polymer.

From the figures it was observed that extraction of all the three metals from coarse fraction was slower than that from fine fraction, even though the concentration gradient available was more in coarse fraction (since metals are more abundant in coarse fraction). One reason for this is the less contact area due to large size of coarse particles. Another reason for this is the poor physical separation of metal from polymers when the particles are large in size. The solvent molecules take more time to penetrate through large particles. So 24 hours was not sufficient for complete extraction in the case of coarse fraction (except in the case of Pb), whereas the extraction was almost complete for fine fraction within 24 hours.

3.2 Effect of Temperature

The recovery of metals was found to increase with rise in temperature from 28⁰C to 50⁰C. But the maximum possible temperature of extraction is limited by the presence of various polymers in PCBs, as the rise in temperature can cause health impacts due to the products formed by partial degradation of polymers. Moreover at 50⁰C, for an extraction time of 24 hours, a recovery of ~ 90% could be achieved for extraction of all the three metals from fine fraction and Cu extraction from coarse fraction. So the temperature of 50⁰C was selected.

3.3 SEQUENTIAL EXTRACTION

To improve the efficiency of extraction, stage wise extraction or sequential extraction was conducted. In each stage, fresh solvent is added to the solid and hence the concentration gradient is increased which improves the efficiency of extraction.

The percentage removals of metals obtained by 2 stages and 3 stages sequential extraction conducted at 50°C are given in Table 2. Metal removal from both fine and coarse fractions, in sequential extractions were found to be better than single stage extraction for 12 hours. This is because in each stage, the driving force available for the metal to enter the solution, ie., the concentration gradient, is more compared to single stage extraction. In single stage extraction the solid is in contact with the same solution and since the metal concentration in the solution is increasing with time the driving force available for extraction is decreasing. But in sequential extraction, where fresh solvent is used in each stage, the solid is coming into contact with the fresh solvent, in which the metal concentration is zero, in each stage. Hence the removal of metal was improved in sequential extraction by improvement in the available driving force, even though the same quantity of solvent was used in both single stage and sequential extractions.

Table 2 Comparison between percentage removals of metals achieved by sequential and single stage extractions

Sample	No.of stages	Percentage removal of		
		Cu	Pb	Zn
Fine	1	89.5	78.44	73.9
	2	95.8	89	95
	3	98	92	96
Coarse	1	70	33.5	42.2
	2	77.85	44	44
	3	79	54	47

3.4 Selective Extraction of Metals

It was observed that the removal of Cu and Zn was slower for coarse fraction compared to fine, and extraction of Cu and Zn was observed to be low at 28°C while that of Pb was not much affected by low temperature. Hence, to check the possibility of selective separation of the metals extraction was conducted at 28°C for 5 hours and after replacing the extract by fresh solvent it was continued for 3 more hours at 50°C. The composition of the extracts after 5 hours and 3 hours are given in Table 3. The results indicate that an extract with relatively pure (98.5%) Pb content was obtained after 5 hours of extraction of coarse fraction at 28°C. In the

extract obtained after 3 hours of extraction of the residual solid under the same conditions, though Pb was still high (85%), significant amount of Cu (13.9%) was also present.

Table 3 Composition of extract formed by series of extraction at 28°C

	Weight percentage in extract		
	Cu	Pb	Zn
After 1 st stage of 5 hrs	0.87	98.5	0.65
After 2 nd stage of 3 hrs	13.9	85	1.1

3.5 Adsorption of metals from extract using alkali treated palm leaf powder

Further studies were conducted to study the removal of metals from the acid extract by biosorption with alkali treated palm leaf powder. The results are shown in Figures 4, 5 and 6.

For all the metals there was a steep reduction in residual concentration initially and after 2 hours there was no significant reduction in residual concentration. This is because initially the availability of active sites is more and hence metals can easily bind to these active sites. As time progresses, since the number of available active sites reduces, the binding of metals becomes more difficult. Driving force for adsorption also reduces with time as the metal concentration in the extract reduces and that on the adsorbent surface increases. Hence adsorption reduces with time (Elangovan et al., 2008)

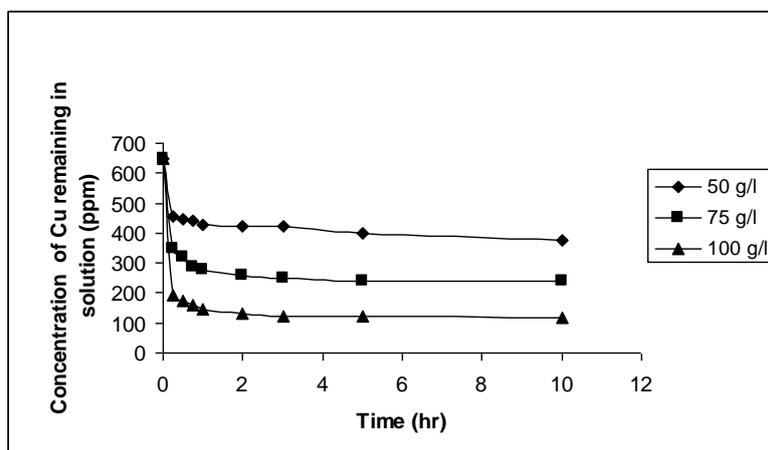


Fig. 4 Variation in concentration of Cu in extract with time of adsorption with alkali treated palm leaf powder

The concentration of Cu in the extract reduced to 0.71 times that of initial concentration (29 % removal) in the first 15 minutes of adsorption with an adsorbent dose of 50 g/l. The residual concentration became 0.53 times and 0.29 times of the initial concentration for adsorbent doses of 75 g/l and 100 g/l respectively. The total removal of Cu was observed to be 42%, 63% and 82% with adsorbent doses of 50, 75 and 100 g/l respectively in 10 hours of adsorption. With high adsorbent dose the adsorption was observed to attain equilibrium faster.

In the case of Pb (Fig. 5) the initial reduction in residual concentrations were 55%, 29% and 10% of the initial concentration of Pb in the extract, for adsorbent doses of 50,75 and 100 g/l respectively. The total removal of Pb obtained in 10 hours of adsorption was estimated to be 69%, 91% respectively for adsorbent doses of 50 and 75 g/l. For 100 g/L of adsorbent dose, Pb was found to be removed completely from extract and this complete removal was achieved in the first 1 hour of adsorption itself.

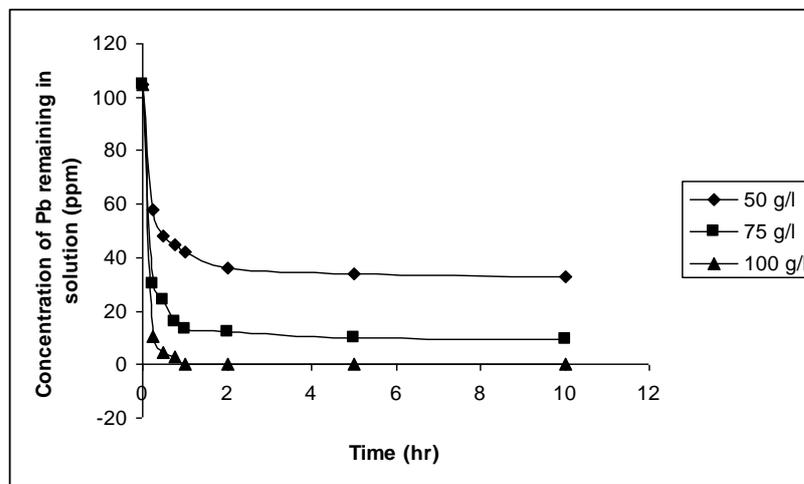


Fig. 5 Variation in concentration of Pb in extract with time of adsorption with alkali treated palm leaf powder

The removal of Zn from extract by adsorption at pH 4 was found to be less. The maximum removal was 32% (31% achieved in first 2 hours) and this was obtained with an adsorbent dose of 100 g/l. The removal achieved in 10 hours of adsorption was 22% (only 13% removal in first 2 hours of adsorption) and 26% (23% removal was achieved in first 2 hours) for adsorbent doses of 50 g/l and 75 g/l respectively.

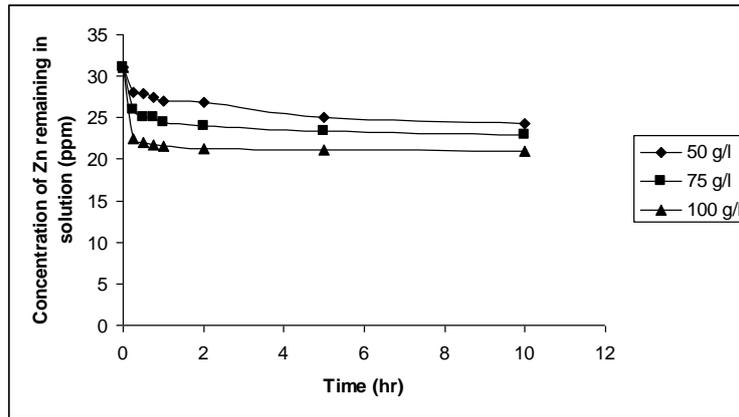


Fig. 6 Variation in concentration of Zn in extract with time of adsorption with alkali treated palm leaf powder

3.6 Adsorption Equilibrium

To estimate the adsorption capacity, equilibrium data were fitted to the well known Langmuir and Freundlich isotherm model. The linearised form of the Langmuir and Freundlich isotherm are given below (Pakshirajan and Swaminathan,2000)

Langmuir:

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

Freundlich:

$$\ln q_e = (1/n) \ln C_e + \ln k_f$$

where, q_e – amount of adsorbate removed from solution at equilibrium (mg/g)

C_e – equilibrium concentration of adsorbate in the solution (mg/l)

Q_{max} – mass of adsorbed solute required to saturate unit mass of adsorbent (mg/g)

b – constant that represent the energy or net enthalpy of adsorption (l/mg)

k_f – Freundlich constant indicative of the adsorption capacity of the adsorbent (mg/g)

n – experimental constant indicative of the adsorption intensity of the adsorbent

Figures 7 and 8 show the Langmuir and Freundlich plots for the adsorption of Cu from extract.

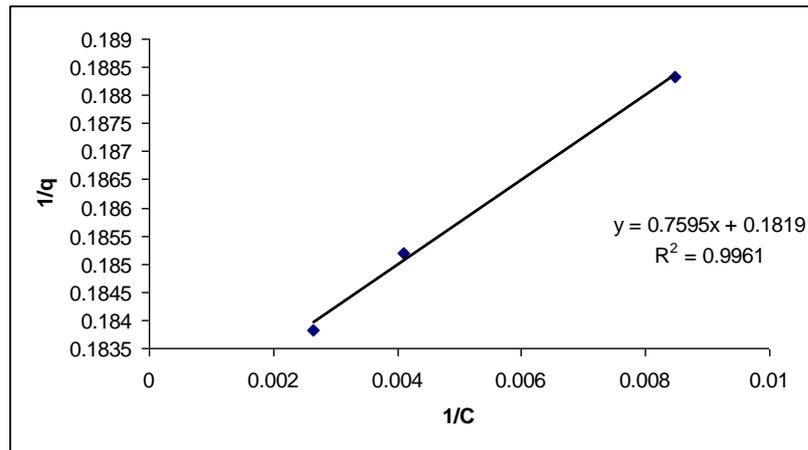


Fig. 7 Langmuir plot for the adsorption of Cu from extract with alkali treated palm leaf powder

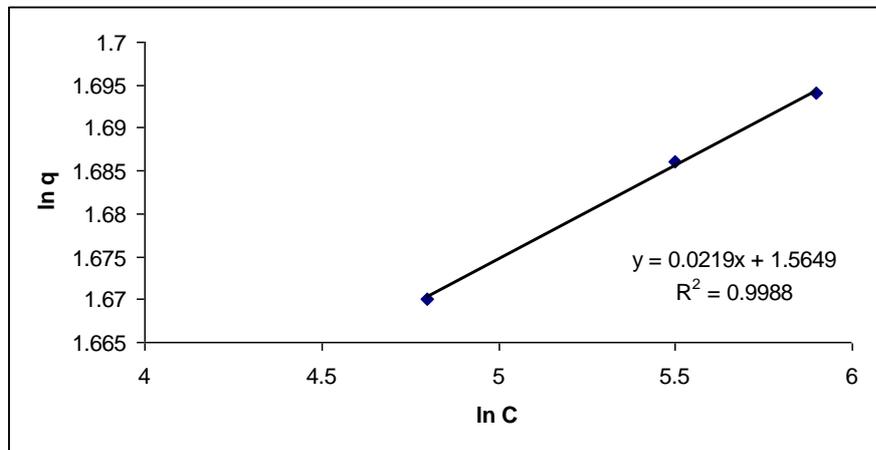


Fig. 8 Freundlich plot for the adsorption of Cu from extract using alkali treated palm leaf powder

Table 4 shows the Freundlich and Langmuir isotherm constants calculated from the corresponding plots. For adsorption of Cu, the isotherm data were fitted well with both Langmuir and Freundlich models, which is evident from the high R^2 values.

Table 4 Freundlich and Langmuir isotherm constants calculated for adsorption of Cu from extract using alkali treated palm leaf powder

Model	Adsorbate	k_f (mg/g)	1/n	R^2
Freundlich	Cu	4.76	0.02	0.9988
		Q_{max} (mg/g)	b (L/mg)	
Langmuir	Cu	5.5	0.2395	0.996

4. Conclusions

The results of this paper clearly prove that it is feasible to develop an eco-friendly method for treatment of e-wastes through application of acid extraction and biosorption. The major findings of this study are summarised below.

- Substantial extraction of Cu, Pb and Zn from powdered waste PCB scraps was achieved at optimized conditions of 2N acid, 50°C and 24 hours.
- Two stage and three stage sequential extractions, under the optimized conditions were found to improve the efficiency of extraction of metals from powdered waste PCB scraps. Cu removal increased by 6.3% and 8.5% in two and three stage extractions respectively. For Pb removal the increase was 10.56% and 13.56% respectively for two and three stage extractions and Zn removal increased by 21.1% and 22.1% for two and three stage extractions respectively.
- Adsorption using alkali treated palm leaf powder was able to give reasonable removals of Cu and Pb.
- Langmuir and Freundlich models were observed to fit the equilibrium data well for the adsorption of Cu from extract using alkali treated palm leaf powder and the model parameters were calculated using linearized equations.

5. References

1. I.O.Ogunniyi, M.K.G.Vermaak and D.R.Groot, (2009), "Chemical composition and liberation characterization of printed circuit board comminution fines for beneficiation investigations", *Waste Management* 29, 2140-2146.
2. Leung AOW, Luksemburg W J, Wong A S and Wong M H, (2003) 'Spatial distribution of Polybrominated Diphenyl Ethers and Polychlorinated Dibenzo-p-dioxins and Dibenzo furans in soil and combusted residue at Guiyu, an electronic waste recycling site in SouthEast China', *Environment Science and Technology* 41 (8), 2730-2737.
3. P.Elangovan, L. Philip and K. Chandaraj, (2008) 'Biosorption of hexavalent and trivalent chromium by Palm flower (*Borassus aethiopum*)', *Chemical Engineering Journal*, 141, 99-111.
4. K.Pakshirajan and T.Swaminathan, (2000) Heavy metal removal by biosorption using *Phanerochaete chrysosporium*. Proc. 41st Annual Conference of the Association of Microbiologist of India, Jaipur.