Lead ion sorption capacity and the structural properties of the humic acid extracts from evergreen forests of different agro-ecological zones of Kerala Western Ghats

Abstract

Forest soils are enriched with soil carbon content. The vegetations and precipitations influences it's chemical structure. The chemical structure directly contributed to it's entire properties. Physico-chemical properties plays a vital role in it's soil functioning. The study was conducted in the humic acid extract of evergreen forest of different agro-ecological zones of Kerala. Determined the chemical structural vartiations and properties of the humic acid extract followed by determined the sorption capacity of the material with lead ion. The study revealed the higher percentage of adsorption of lead ion with humic acid extract from evergreen forest of northern high hills – charnockite zone of western ghats of Kerala. This was the combined effect of enhanced cation exchange capacity and –COOH acidity of the material.These chemical structure and the functional properties to the sorption capacity of the humic acid extract to chelate the lead ion was evaluated .The higher cation exchange capacity and the –COOH acidity favoured the lead ion adsorption.Adsorption isotherm modeling was revealed the multilayer and monolayer adsorption od lead ion on humic acid depends with the heterogeneity of the HA surfaces. Maximum amount of lead ion molecule adsorbed on the HA surface was observed for humci acid from SHH-K agro-ecological zone.

***Key word**: Humic acid, Extraction, Cation exchange capacity, Acidity Sorption*

1. INTRODUCTION

Humic acids constitute a family of soil organic matter that exhibit an ubiquitous presence and a broad spectrum of structural variations. The material plays prominent role in soil nutrient capacity and structural stability[1]. Heterogeneity of it's structure relate with the factors like vegetation, climatic conditions and mineralogical aspects of the particular area[2]. Humic acid (HA) is a derivative of decomposed organic material that is soluble in alkali conditions and insoluble in acidic condition. A chemical structure of HA consist of carbon aromatic rings with di- or tri-hydroxyl phenols attached by -O-, -NH-, -N-, - S-, and contain -OH group and quinone (O- C6H4-O-) groups. Distinguishing the structural change in accordance with the physico-chemical properties of the humic acid,which are played an important role on soil system functioning[3]. Western Ghats of Kerala have an enriched biodiversity and humid tropic climate.The variations among the vegetative occupancy and the precipitation definitely affect the chemical structure of the material there by it's functional properties. The study aims to evaluate the structural variations of humic acid extract from evergreen forest systems of different agro-ecological zones of Western Ghats , Kerala .The work couple with spectroscopic analysis instead of the chemical properties of the humic acid extract.

2. MATERIALS AND METHODS

Humic acid (HA) was extracted from the soils of evergreen forest systems from northern high hills- charnockite (NHH-C),southern high hills –khondalite (SHH-K) and Wayanad plateau –granite synite(WP -G) regions of Kerala. The extraction and the purification of HA was done by acidic precipitation with 6 M HCl and 1 M NaOH [4] followed by dialysis using visking dialysis tube and performed the HF/HCl treatment[5]. The UV-Visible spectrum of the samples were probed inusing0.05 M NaHCO3 in the range of 200-800 nm wavelength (Varian, Cary 5000). Fourier-transform Infrared spectra was recorded with a resolution of 4 cm-1 at 4000-400 cm-1 using KBr pellets (Thermo Nicolet, Avatar 37). The cation exchange capacity of the samples were determined by barium acetate saturation method. The total acidity and the -COOH acidity were determined by titration with barium hydroxide followed by potentiometric estimations.The percentage of carbon was determined using a CHNS analyser

The adsorption studies of the humic acid extracts with lead ion was examined by the batch adsorption at temperature 35^0 C, and pH=4 .Prepared the heavy metal ion solutions at 10 ppm,15 ppm ,20 ppm,25 ppm,30 ppm,35 ppm,40 ppm concentrations (30 mL) and taken the adsorbent at 2 gm of humic acid extracts at 150 rpm incubating shaker speed with the time period of 24 hrs. After the required time taken the equivalent concentration and calculated the percentage of adsorption.

Adsorption isotherm models were carried out to study the type of adsorption of lead ion on humic acid surface either be monolayer or be multilayer. Langmiur model and Freundlich models were examined with the data of the adsorption . The Langmiur isotherm model,showing the monolayer adsorption on adsorbate on adsorbent represented by the following equation ,

$$C_e/q_e=1/K_Lq_{max} +C_e/q_{max} \text{ --------------------------------------(Eq1)}$$

where,C_e (mg/L) and q_e (mg/g) are the concentrations of the molecules at the equilibrium and the amount of adsorbed molecule on the surface of the adsorbent at any time,respectively. K_L represent the Langmiur constant (L/mg).

Freundlich model was performed to evaluate the possibility of multilayer adsorption on lead ion on humic acid extract surfaces. The model is represented by

$$\text{Log } q_e = \log K_F + 1/n \log C_e \text{ -------------------------------------(Eq2)}$$

where, q_e (mg/g) represents the adsorbed molecule, C_e (mg/L) is the equilibrium concentration of the molecule, n represents the Freundlich constant and K_F denotesthe Freundlich exponent.

3. RESULS AND DISCUSSION

The UV-Visible spectrum(Fig.1) of humic acid extracts showed the characteristic peaks corresponding to $\pi - \pi^*$ transitions in the range of 230 – 290 nm. This shoulder region were the characteristic of conjugated quinine or ketones.The absorbance versus wavelength curves were monotonically decreases with increase of wavelength. The E_4 /E_6 ratio was observed in the range of 1.01 – 1.42.Higher ratio was observed for humic acid extract from evergreen forest of WP-G zone(1.42). The humic acid from evergreen forest of NHH-C and SHH-K determined with the E_4 /E_6 ratio of 1.23 and 1.01 respectively. So HA from WP-G was considered with lowest stable humic acid compared with the others [6]. The fourier transformation infra-red spectroscopy analysis revealed the presence of core functional groups and the impurities associated with the humic acid extract formed from process p1(Fig 4).The HA extract samples were showed the characteristic peaks at 3400-3300 cm^{-1} ,2970-2840 cm^{-1} ,1710-1715 cm^{-1} ,1620-1640 cm^{-1},1380-1386 cm^{-1},1220-1226 cm^{-1} , 1100-1050 cm^{-1} and 800-500 cm^{-1} corresponded to the –OH stretching, aliphatic –CH stretching [7],-C=O stretching of COOH and ketones,-C=O of H bonded conjugated ketones,-OH deformation and C-O stretching of phenolic OH,C-O stretching and OH deformation of COOH,C-O stretching of polysaccharide and the inorganic impurities associated as silicate bonds [8].

a	b	c

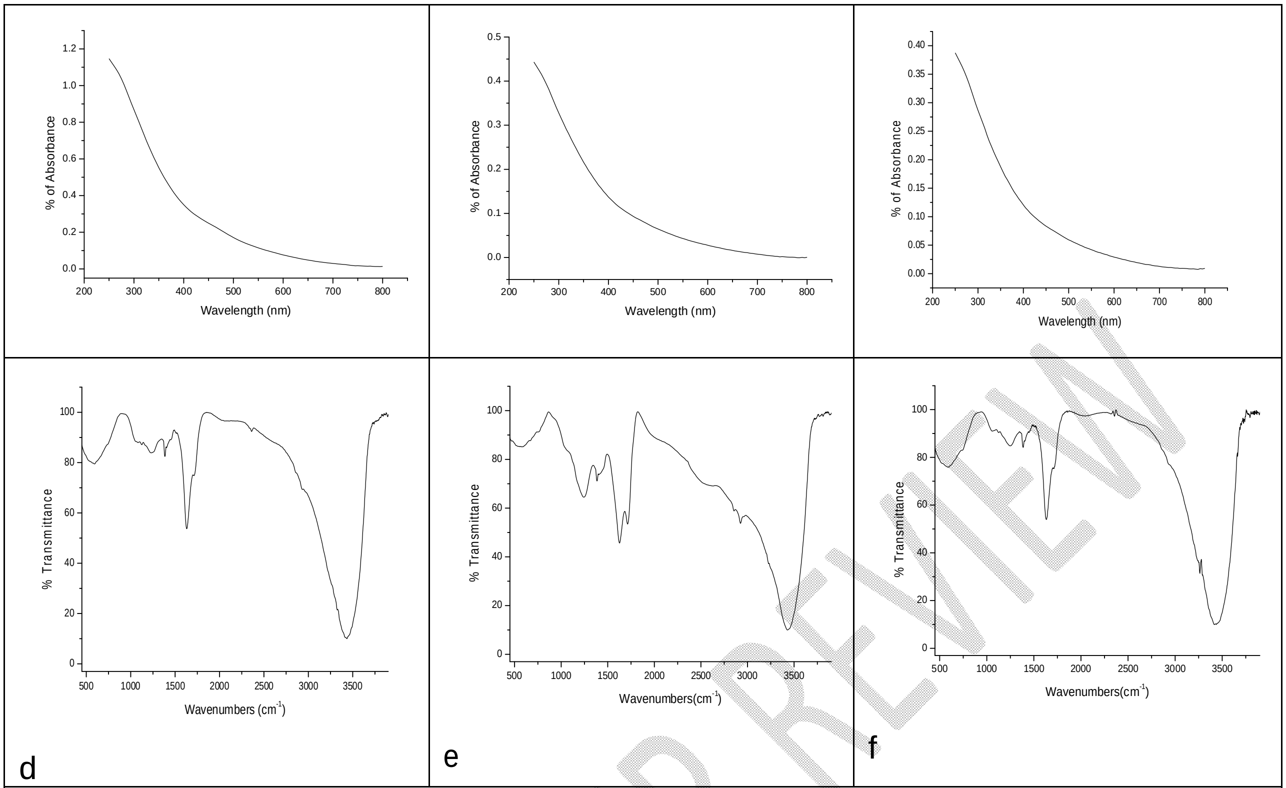


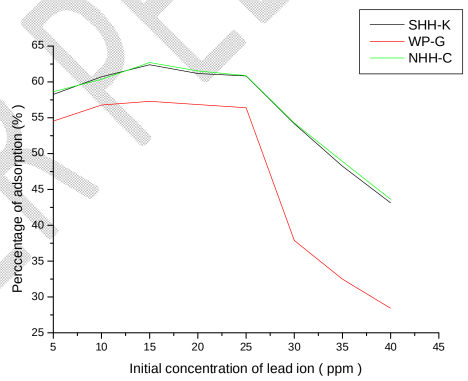
Figure 1. UV-Visible spectrum of the humic acid extract from evergreen forests (a) NHH-C,(b) SHH-K,(c) WP-G and FTIR spectrum of the humic acid extract from evergreen forest (d) NHH-C,(b) SHH-K,(c) WP-G.

The physico-chemical parameters of the humic acids extracted from evergreen forests of different agro-ecological zones of western ghats of Kerala revealed the performance ability of the material and evaluated their structural dependency on the chemical properties. Elemental carbon percentage analysis by CHNS analyser examined that humic acids from evergreen forest of WP-G have the higher value and the evergreen forest of NHH-C showed the lower value for percentage of carbon.Cation exchange capacity(CEC) examined , higher CEC was observed for humic acid extract from evergreen forest of NHH-C and diminished value for WP-G. Enhanced CEC values,due to the extreme hydration of HAs in evergreen forest of northern high hills-charnockite zone [9]. The better value of CEC helped to improve the soil nutrient ability in a considerable amount.Exchange of elements enhanced the stability of organo-mineral interactions of the forest soil.The carboxylic acidity was in cooperated with cation exchange and organo-mineral complex formation. Higher –COOH acidity was viewed for humic acid from evergreen forest system of NHH-C. Lower value was monitored with humic acid from evergreen forest of WP-G.In case of total acidity ,HA from evergreen forest of NHH-C was evaluated with lower value and humic acid from the same forest type in WP-G showed the lower value. The inverse observation of –COOH acidity and total acidity was the correlation with the phenolic OH content of the humic acid skeleton. The materials showed the higher –COOH acidity have the high solubility in water [10].

Table 1. Physico-chemical properties of the humic acid extracts

Chemical properties	Humic Acid Extract		
	NHH-C	SHH-K	WP-G
Elemental carbon percentage	52.14	52.71	53.85
Cation exchange capacity	456.78	443.85	437.34
-COOH acidity	368.19	359.26	348.58
Total acidity	682.47	685.77	684.07

The adsorption studies revealed that higher percentage of adsorption was observed with humic acid extract from evergreen forest of NHH-C.It was contributed by the higher cation exchange capacity and –COOH acidity [11] .The H^+ ion transfer from humic acid skeleton promoted the Pb^{2+} ion linkage with the humic acid structures [12]. In 15 ppm concentration of lead ion in whole the adsorption conditions, percentage of adsorption was higher compared with the other initial concentrations. After this concentration, percentage of adsorption was decreased due to the unavailability of site for lead ion sorption on the surfaces of humic acid extract[13].



a

Figure 2. Percentage of adsorption of heavy metals on humic acid extract (a) lead ion

Adsorption isotherm modeling was revealed the type of adsorption of lead ion on humic acid(Fig.3). Compared with the two adsorption isotherm models, langmiur and freundlich model, freundlich model was showed the best fit model for lead ion adsorption on humic acids from NHH-C and WP-G agro-ecological zones.So it explained the possibility of multilayer adsorption(Tab.2). From the value of n from freundlich model, value which was greater than one confirmed the more than two or three layer adsorption of lead ion was taking place in the humci acid extract surfaces of NHH-C and WP-G. But for SHH-K, monolayer adsorption of lead ion was predicted by the fit with langmiur with R^2 value of 0.92 . In the humic acid extracts, amount of lead ion molecules adsorbed on NHH-C , SHH-K and WP-G were 0.0022 mg/g ,0.0047 mg/g ,0.0021 mg/g.

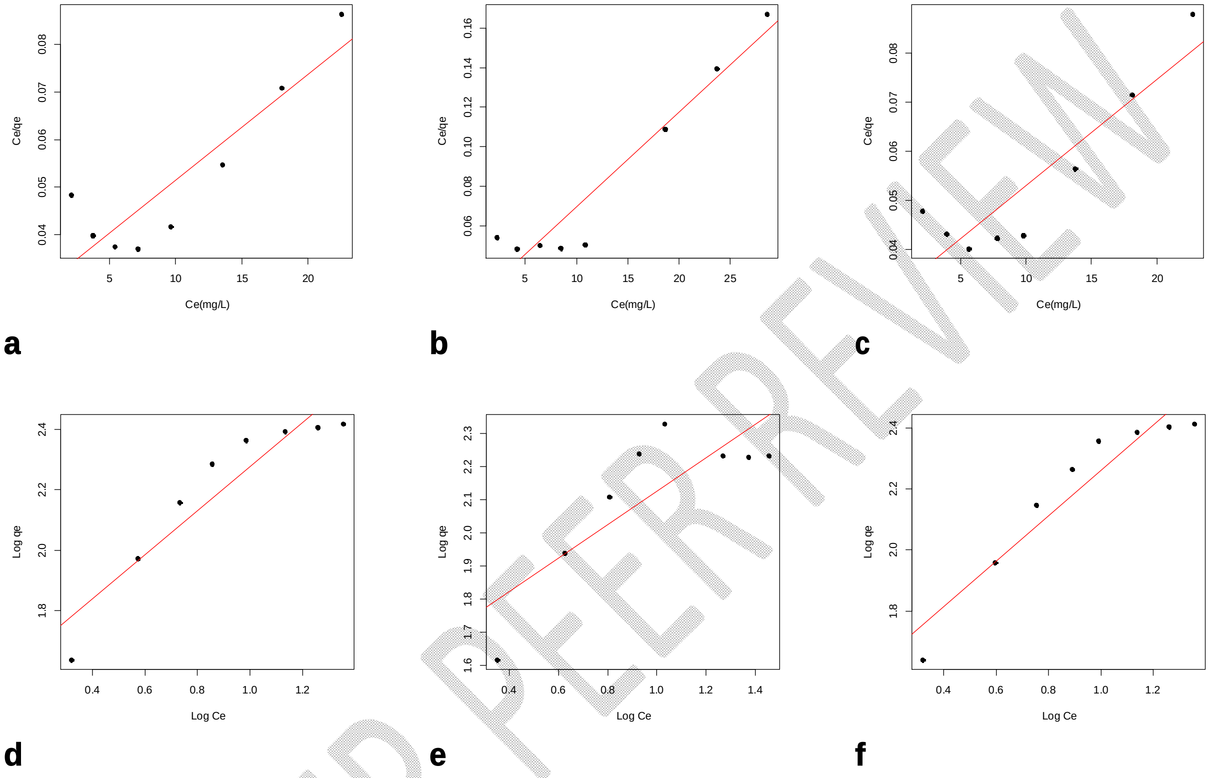


Figure 3. Adsorption isotherms of lead ion adsorption on humic acid extract.Langmiur model (a)NHH-C,(b) SHH-K,(C) WP-G and Freundlich model(d) NHH-C,(e) SHH-K,(f) WP-G

Table 2. Adsorption isotherm parameters of lead ion adsorption on humic acid extract

Lead ion adsorption on humic acid extract	**Langmuir model**			**Freundlich model**		
	R^2	qm (mg/g)	KL (g/L)	R^2	n	KF(g/L)
NHH-C	0.78	0.0022	0.028	0.85	1.39	4.71
SHH-K	0.92	0.0047	0.021	0.69	1.99	5.09
WP-G	0.82	0.0021	0.0313	0.9	1.34	4.56

4. CONCLUSION

The study concluded the structural , chemical and sorption capacity of humic acid extracts from evergreen forests of different agro-ecological zones of Kerala. Lower stability of the humic acid extract from evergreen forest of WP-G zone . Lower elemental carbon percentage given an idea of prior condensed carbon structures than the long and branched chains of aliphatic carbon structures The properties support the sorption capacity, like cation exchange capacity, -COOH acidity influenced the efficacy of lead ion adsorption .The humic acid extract with enhanced CEC and –COOH acidity was determined for evergreen forest of northern high hills –charnockite zone. And these properties stipulated the percentage of adsorption of lead ion on the surfaces of humic acid extract. Adsorption isotherm modeling studies revealed the type of adsorption of lead ion was varied with the surface parameters of the humic acid and the pore size.

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