

# 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 vegetation and precipitation influences its chemical structure. The chemical structure directly contributed to its entire properties. Physico-chemical properties play a vital role in its soil functioning. The sorption capacity of the humic acid can be applied in the nutrient uptake enhancement and waste water treatment. The study was conducted in the humic acid extract of evergreen forest of different agro-ecological zones of Kerala. Extraction was done by the acidic precipitation method recommended by International Humic Substance Society (IHSS). Determine the chemical structural variations and properties of the humic acid extracts followed by determining 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 of 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 humic acid from SHH-K agro-ecological zone. This method can be considered as economically viable green method for looking forward technology for waste water treatment.

**Key word:** *Acidity, Cation exchange capacity, Extraction, Humic acid, 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 a prominent role in soil nutrient capacity and structural stability[1]. Heterogeneity of its structure relates 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 conditions. A chemical structure of HA consists of carbon aromatic rings with di- or tri-hydroxyl phenols attached by -O-, -NH-, -N-, -S-, and contain -OH group and quinone (O-C<sub>6</sub>H<sub>4</sub>-O-) groups. Distinguishing the structural change in accordance with the physico-chemical properties of the humic acid, which play an important role in soil system functioning[3]. The properties of humic acid is vast and includes moisture retention capacity, cation exchange capacity[4], buffering capacity, chelation property[5]. These properties coupled with the organo mineral interactions of the soil. This mineral interaction promotes the nutrient uptake by the plants and increases the crop yield. Recent studies reported the interaction of humic acid with clay minerals, plant hormones and nano materials. The hype of nano science in the area of soil science also be applicable to enhance the agricultural systems and environmental remedial activities.

Western Ghats of Kerala have an enriched biodiversity and humid tropic climate. The climatic conditions are varied in different agro-ecological zones. Western Ghats of Kerala is mainly occupied by the red soils, laterites, black soil and humid soil. This heterogeneity will reflect the structure of the humic acid also. The variations among the vegetative occupancy and the precipitation definitely affect the chemical structure of the material thereby its functional properties. The lack of adequate studies on the ecology of the humic acid of Kerala Western Ghats region is the major challenging of understanding its functionality. 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 coupled 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 syenite (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 a visking dialysis tube and performed the HF/HCl treatment[5]. The UV-Visible spectrum of the samples were probed using 0.05 M NaHCO<sub>3</sub> in the range of 200-800 nm wavelength (Varian, Cary 5000). Fourier-transform Infrared spectra were recorded with a resolution of 4 cm<sup>-1</sup> at 4000-400 cm<sup>-1</sup> 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° 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 a humic acid surface either be monolayer or multilayer. Langmuir models and Freundlich models were examined with the data of the adsorption. The Langmuir isotherm model, showing the monolayer adsorption on adsorbate on adsorbent represented by the following equation,

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

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

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

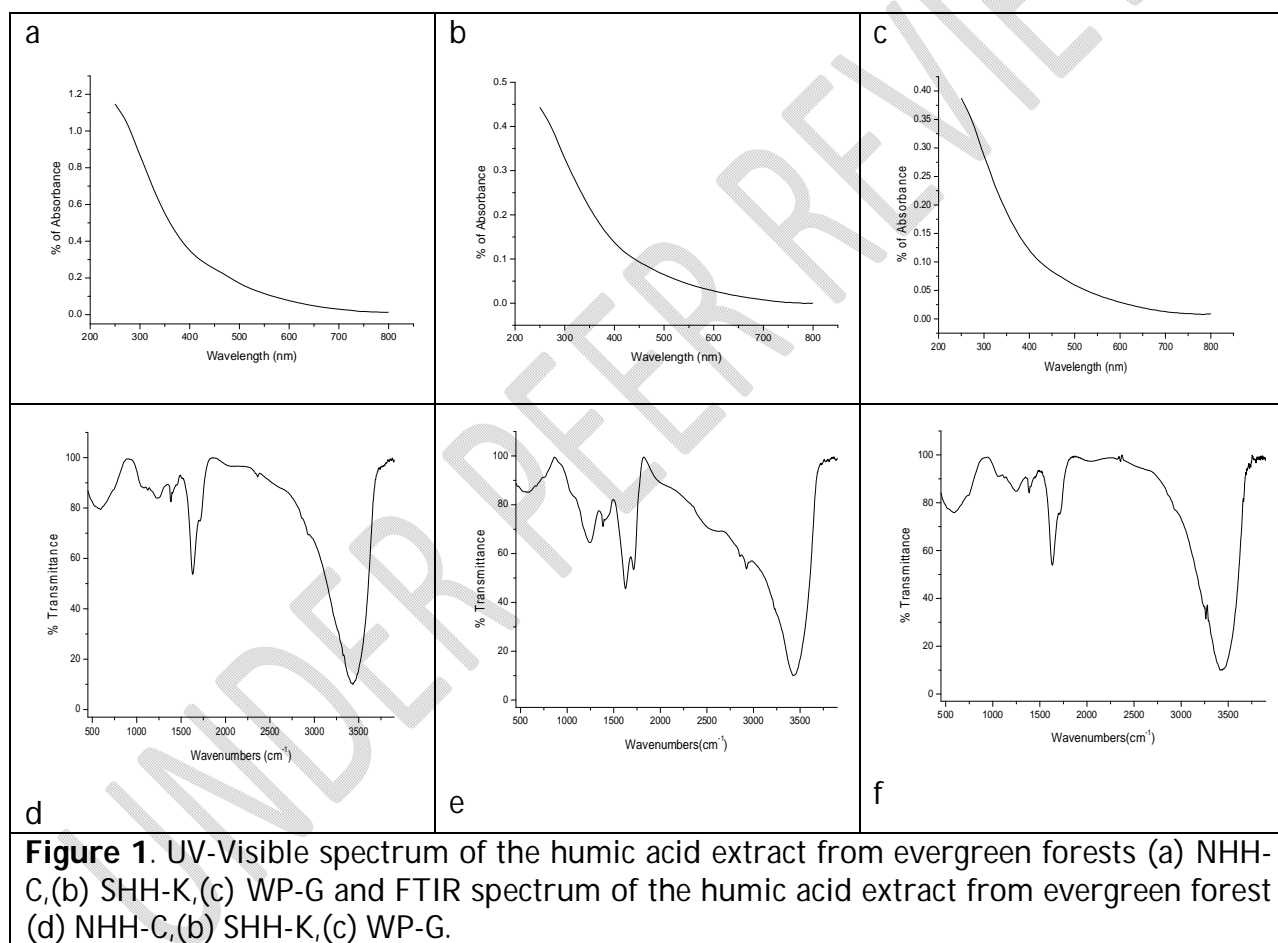
$$\text{Log } q_e = \text{log } K_F + 1/n \text{ log } C_e \text{-----(Eq2)}$$

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  $K_F$  denotes the Freundlich exponent.

### 3. RESULTS 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 was the characteristic of conjugated quinone or ketones. The absorbance versus wavelength curves were monotonically decreasing 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 forests of WP-G zone (1.42). The humic acid from evergreen forest of NHH-C and

SHH-K is 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 1).The HA extract samples were showed the characteristic peaks at  $3400-3300\text{ cm}^{-1}$ ,  $2970-2840\text{ cm}^{-1}$ ,  $1710-1715\text{ cm}^{-1}$ ,  $1620-1640\text{ cm}^{-1}$ ,  $1380-1386\text{ cm}^{-1}$ ,  $1220-1226\text{ cm}^{-1}$ ,  $1100-1050\text{ cm}^{-1}$  and  $800-500\text{ cm}^{-1}$  corresponded to the  $-\text{OH}$  stretching,aliphatic  $-\text{CH}$  stretching[7],  $-\text{C}=\text{O}$  stretching of COOH and ketones,  $-\text{C}=\text{O}$  of H bonded conjugated ketones,  $-\text{OH}$  deformation and  $\text{C}-\text{O}$  stretching of phenolic OH,  $\text{C}-\text{O}$  stretching and  $\text{OH}$  deformation of COOH,  $\text{C}-\text{O}$  stretching of polysaccharide and the inorganic impurities associated as silicate bonds[8].



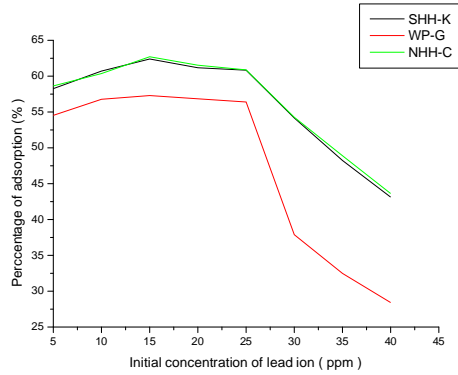
The physico-chemical parameters of the humic acids extracted from evergreen forests of different agro-ecological zones of Western Ghats of Kerala revealed the performance ability of the material and evaluated their structural dependency on the chemical properties. Elemental carbon percentage analysis 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 influence of humic acid on the cation exchange capacity of the soil was discussed by Soares [10]. The carboxylic acidity was in cooperation with cation exchange and organo-mineral complex formation [11]. 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 [12]. The materials showed the higher  $-COOH$  acidity has the high solubility in water [13].

**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

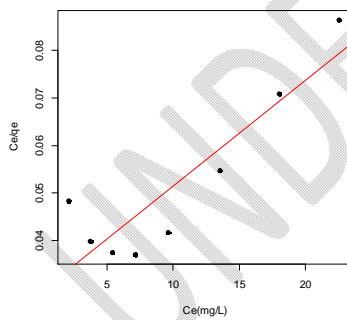
The adsorption studies revealed that higher percentage of adsorption was observed with humic acid extract from evergreen forest of NHH-C [14]. It was contributed by the higher cation exchange capacity and  $-COOH$  acidity [15]. The  $H^+$  ion transfer from humic acid skeleton promoted the  $Pb^{2+}$  ion linkage with the humic acid structures [16]. In 15 ppm concentration of lead ion in whole the adsorption conditions, the percentage of adsorption was higher compared with the other initial concentrations. After this concentration, the percentage of adsorption was decreased due to the unavailability of sites for lead ion sorption on the surfaces of humic acid extract [17]. Adsorption of cadmium ion on humic acid coated with titanium dioxide was showed the decreasing in adsorption percentage when the concentration of the cadmium ion attained above the concentration of 100 ppm [18].



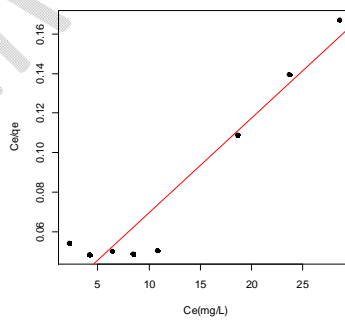
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**Figure 2.** Percentage of adsorption of heavy metals on humic acid extract (a) lead ion

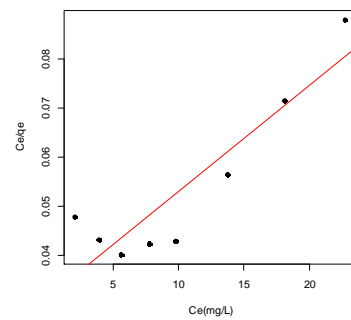
Adsorption isotherm modeling revealed the type of adsorption of lead ions on humic acid (Fig.3). Compared with the two adsorption isotherm models, Langmuir and Freundlich model, the Freundlich model was shown to be the best fit model for lead ion adsorption on humic acids from NHH-C and WP-G agro-ecological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



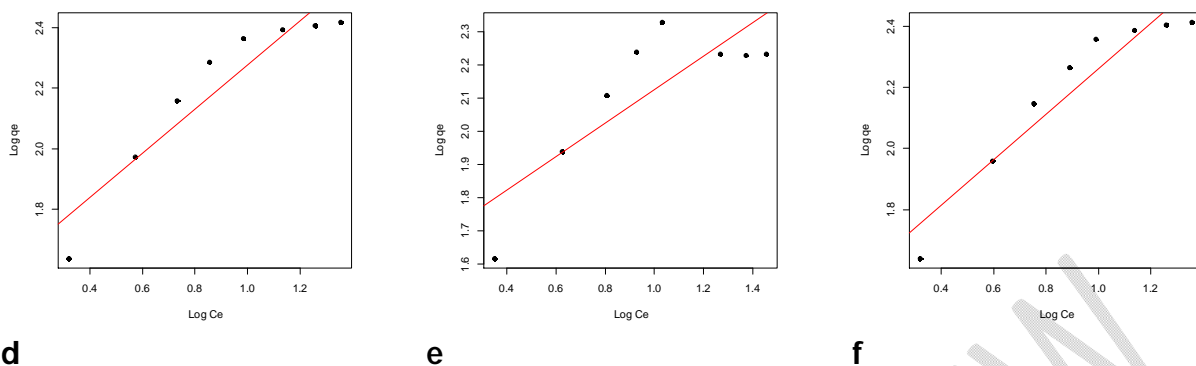
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c



**Figure 3.** Adsorption isotherms of lead ion adsorption on humic acid extract. Langmuir 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 ions on the surfaces of humic acid extract. Adsorption isotherm modeling studies revealed the type of adsorption of lead ions was varied with the surface parameters of the humic acid and the pore size.

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