

Adsorption of cadmium ion on humic acid extracted from laterite soils of Kannur district, Kerala

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Abstract— Humic acids are highly stable and functionalized portions of soil organic matter. Because of its structural heterogeneity and surface porosity, it act as a catalyst in soil nutrient enrichment and plant growth. Besides, humic acid sequester the heavy metal ions on its surfaces by pore filling and multilayer adsorption. The study focused the structural behavior and the physico-chemical properties of the humic acid extracted from the laterite soils of Kannur district of Kerala. And evaluated the sorption performance of the humic acid with cadmium ion. Efficacy of the removal of the cadmium ion by humic acid will leads to an green technology for water purification and the sustainable use of the natural resources.

Keywords— Humic Acid, Extraction, Infra-Red Spectroscopy, Cation Exchange, Capacity, Adsorption.

I. INTRODUCTION

The importance of humic substances are because of the organic carbon content and the effect on soil fertility, soil structure, water acidity, transportation and mineral weathering. Structural variety of this material directly influence the functioning on the soil [1]. Based on the solubility in different pH, the humic substances is classified into mainly three, fulvic acid (soluble in acidic and alkaline conditions), humic acid (soluble in alkaline condition), humin (insoluble in acidic and alkaline conditions). So the extraction of the material deals with the different pH of the extracting solution. From the three compounds, the highly stable and functioning material is humic acid. It is a dark coloured material. The role of humic acid on plant growth and soil nutrient capacity is extensively reviewed [2]. The structure of the humic acid consist of carboxylic group, methenolic group, phenolic group and methoxy groups. The different carbon functionalities create a reaction potential to this molecule. The cation exchange capacity, total and carboxylic acidities and higher surface area are the unique properties of the humic acids. Effect of humic acid on plant root growth, plant growth hormone production, soil nutrient capacity and carbon cycle are documented by previous researchers. Highly porous and macro molecular structures of the humic acid help them to associate with other metal ion through adsorption on the surfaces [3]. Application of the material for environmental and agricultural purposes may increase the potential of the material. Instead of these, using a natural material like humic acid for impurity removal makes a green chemical approach.

The present study investigates the properties and structure of the humic acid extract from laterite soil of Kerala. The study monitors the cadmium ion removal efficacy of the humic acid and looking a forward technology for wastewater treatment.

II. MATERIALS AND METHODS

Soil samples were collected from Kannur district of Kerala. The soils were in laterite structure. Samples were collected from surface to the depth 20 cm. Uniformly mixed the sample and stored in clean bottles for analysis.

2.1 Humic acid extraction

Humic acid was extracted by adding 1 M NaOH and 6 M HCl for precipitation. Precipitated humic acid was purified by membrane vacuum filtration followed by dialysis against deionized water. Humic acid obtained after the purification was dried through freeze dry method. The samples for kept in moisture free atmosphere in clean and dried container.

2.2 UV-Visible spectroscopy

Optical properties of the humic acid was studied using Varian, Cary 5000 UV-Visible spectrophotometer with the range of 200- 800 nm. The sample was prepared by mixing 0.1 mg humic acid to 10 mL of 0.05 M NaHCO₃. Determined the ratio of absorbance at 465 nm to the absorbance at 645 nm (E₄/E₆).

2.3 Fourier Transformation Infra-red spectroscopy

Molecular spectrum of the humic acid was recorded using Thermo Nicolet, Avatar 37 infrared spectrophotometer. The sample was pelletized with KBr powder in the ratio 1:200 for sample to KBr. Spectrum was recorded with the resolution of 4 cm⁻¹ in the range of 4000 to 400 cm⁻¹.

2.4 Elemental analysis

Elemental composition of the humic acid was determined on CHNS elemental analyser, Euro vector CHNS elemental analyser, E A 3000. Relative percentage of the carbon, hydrogen nitrogen was directly measured from the analyser. The percentage of oxygen was determined as the difference hundred with the sum of percentage of C, H, N and sulphur.

2.5 Physico-chemical properties

2.5.1 Cation Exchange Capacity

The cation exchange capacity of the humic acid from laterite soil was determined by barium acetate method. Measured the pH and conductivity at the final stage and calculated the amount of exchangeable cations.

2.5.2 Zero point charge

It was determined the zero point charge of the humic acid by potentiometric titration using 0.1 M HCl and 0.1 M NaOH solution on HANNA, HI901 autotitrator.

2.5.3 Total acidity and –COOH acidity

Total acidity and the carboxyl acidity(-COOH) of HA was measured by barium hydroxide titration method. The –COOH acidity was calculated by the potentiometric titration against calcium acetate. Phenolic –OH acidity was evaluated by the difference of total acidity and the –COOH acidity.

2.6 Adsorption

From the stock solution of Cd²⁺ ion, prepared at different concentrations as 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm, 30 ppm, 35 ppm, 400 ppm. Added the approximate amount (1 mg) of humic acid to 30 mL of selected concentrations of Cd²⁺ ion solution (5-40 ppm) in a Eppendorf centrifuge tube. Experiment was performed at pH 4, 7 and 9 (adjusted the pH of the solution to 4 by adding 0.01 M HCl and 0.01 M NaOH solution) at the temperature 35° C for 48 hrs and the incubating shaker with a speed of 150 rpm. After 24 hrs, aliquot of the solution was centrifuged. Taken the supernatant and analysed on atomic absorption spectrophotometer to calculate the remained cadmium ion concentration after the adsorption. Determined the maximum percentage of Cd²⁺ ion adsorbed and the q_{max} from the following equations

$$\% \text{ of adsorption} = (C_0 - C_e) * 100 / C_0$$

$$q_e = (C_0 - C_e) * V / W$$

where, C₀-initial concentration of Cd²⁺ ion in ppm, C_e-equilibrium concentration of Cd²⁺ ion in ppm, V-volume of solution in litre, W-weight of the adsorbent in mg.

III. RESULTS AND DISCUSSIONS

UV-Visible spectroscopy analysis provided the optical property of the chemical structure, whereas the involvement of chromophores (Fig. 1). It was observed the peak with monotonously decreased with wavelength. The ratio of absorbance at

645 nm to 465 nm, calculated as 2.95. Lower value range of E_4/E_6 , indicated the stability of the material in its existing form [4]. The FTIR spectrum of humic acid consisted of major adsorption bands at $3400\text{--}3300\text{ cm}^{-1}$, $2940\text{--}2900\text{ cm}^{-1}$, $1725\text{--}1700\text{ cm}^{-1}$, $1630\text{--}1600\text{ cm}^{-1}$, $1460\text{--}1440\text{ cm}^{-1}$, $1400\text{--}1375\text{ cm}^{-1}$. These peaks were corresponded to the stretching vibrations of phenolic --OH stretching, C-H stretching of alkanes, C=O stretching of carboxyl groups, aromatic C=C stretching, deformation of C-H bonds of methyl group [5]. The molecular spectrum confirmed the structure of humic acid with the poly carbon functional groups. This heterogeneity of carbon functionalities, make the HA to ubiquitous and potential material in soil organic matter. The decomposition of soil organic matter at various stages caused this heterogeneity in its structure.

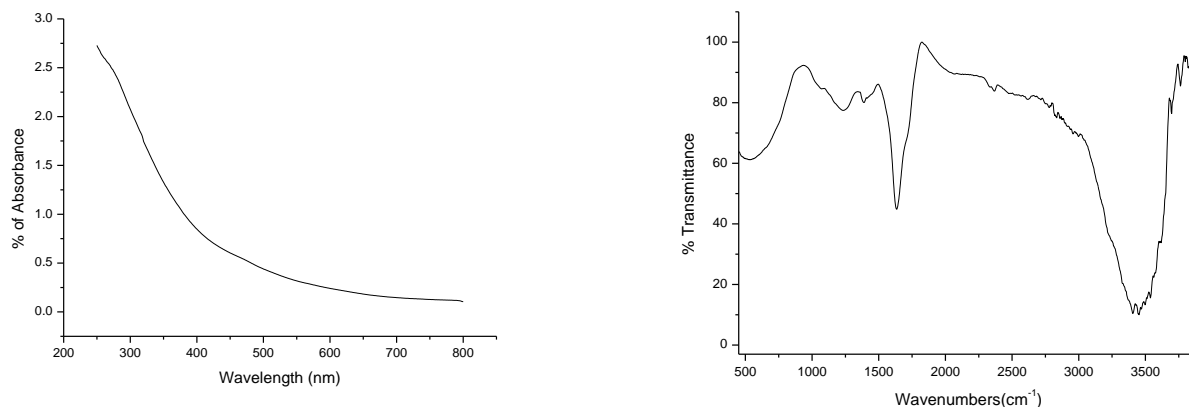


FIGURE 1: Spectroscopic characterization of the humic acid (a)UV-Visible Spectroscopy, (b) FTIR Spectroscopy

The elemental analysis of the humic acid from laterite soil was observed as 64.34 % of carbon, 4.27 % hydrogen, 27.47 % oxygen and 3.92% nitrogen (Table 1). The C/N ratio of the humic acid from laterite soil of Kannur observed with the value 16.41 and the O/C ratio calculated as 0.43. The percentage of carbon content was relatively higher than the reported values for humic acids [6]. It was noted that the humic acid extract from laterite soils were rich in carbon supra-molecular structures and may incorporate the reaction performance of the material.

**TABLE 1
ELEMENTAL COMPOSITION OF HUMIC ACID EXTRACT**

| Humic acid extract from laterite soil | Elemental composition | | | | Ratios | |
|---------------------------------------|-----------------------|--------|---------|--------|--------|------|
| | C | H | O | N | C/N | O/C |
| | 64.34 % | 4.27 % | 27.47 % | 3.92 % | 16.41 | 0.43 |

3.1 Physico-chemical properties

Cation exchange capacity of the humic acid was observed as 473. 61 meq/100 gm (Tab. 2). The value of CEC predicted the efficacy of the material to exchange the inorganic ions a, thereby promote the soil nutrient capacity [7]. By binding with the clay minerals, to form organo-mineral complexes and perform wide varieties of duties to the soil systems. The zero point charge (ZPC) of the humic acid was observed as 3. 42. Above the pH of 3. 42, HA favors the positively charged ions (cations) and below this pH it favours the anion adsorption on its surface [8]. Too acidic condition (below 3. 42) the net surface charge of the molecule is negative and attract to the positively charged species to its surface and forms the bonding. The total acidity and the --COOH acidity were evaluated as 719. 09 cmol/Kg and 436. 28 cmol/Kg respectively. The component --COOH acidity, determines the ability to chelate with the ions by releasing H^+ ion and bind with the metal ions and the cations like Na^+ , K^+ etc [9].

TABLE 2
PHYSICO-CHEMICAL PROPERTIES OF HUMCI ACID EXTRACT

| Properties | |
|--------------------------|-------------------|
| Cation Exchange Capacity | 473.61 meq/100 gm |
| Zero Point Charge | 3.42 |
| Total Acidity | 719.09 cmol/Kg |
| Carboxylic Acid Acidity | 436.28 cmol/Kg |

3.2 Adsorption studies

Adsorption of cadmium ion on humic acid from laterite soil indicated the potential of HA to heavy metal chelation (Fig. 2). It was observed that, percentage of adsorption of cadmium ion increase upto the initial concentration of 10 ppm of Cd^{2+} ion as 59.73%. Where the q_{max} was obtained for 25 ppm initial concentration as 212.7 mg/Kg. The initial concentration increased, the percentage of adsorption increased upto the initial concentration of 10 ppm then decreased to 28.56% at 40 ppm of initial concentration of Cd^{2+} ion. When the pH of the solution increased from 4 to 9, the maximum percentage of adsorption was observed at 10 ppm initial concentration of Cd^{2+} ion and the values observed as decreased from 59.73% to 56.27% (pH 7) and 53.28% (pH 9). The value of q_{max} observed as observed for pH 7 and pH 9 were 192.63 mg/Kg and 180.22 mg/Kg. Observation of sorption behavior of the humic acid related with its carboxylic acid functional group, which directly associated with the Cd^{2+} ions of the aqueous solution [10, 11]. The cation exchange capacity also catalyzed the adsorption mechanism of cadmium ion on the surfaces of extracted humic acids from laterite soils of Kerala [12].

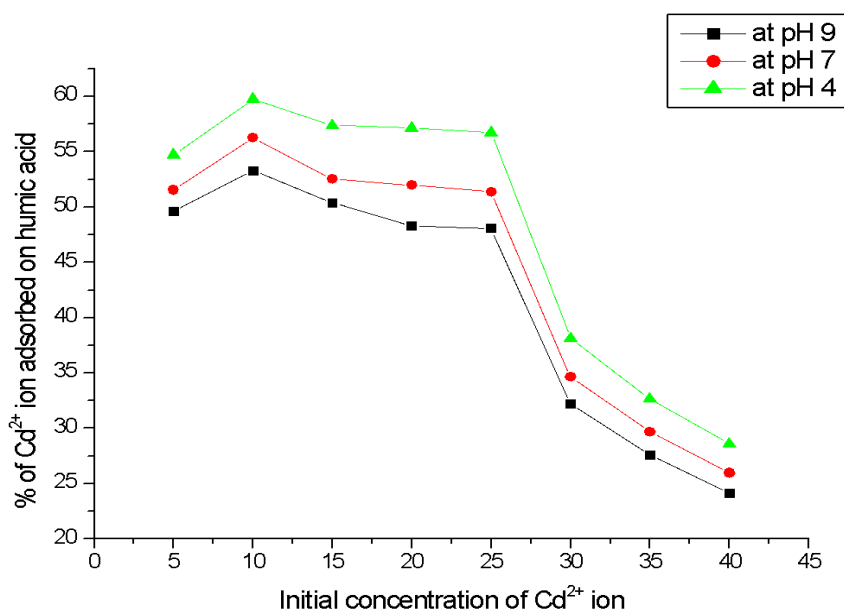


FIGURE 2: Percentage of Cd^{2+} ion adsorption on humic acid at different pH

IV. CONCLUSION

The humic acid extracted from laterite soil, Kannur is consisted with carbon function groups such as phenolic, carboxylic, ketonic and carbon ring structure. The stability of the material indicates the highly stable material with good cation exchange capacity and $-\text{COOH}$ acidity. The supramolecular carbon dominated species have the potential to remove the heavy metal ion, cadmium. Lower initial concentration favours the maximum percentage of adsorption of Cd^{2+} ion and relatively higher initial concentration of Cd^{2+} ion leads the higher q_e value. The percentage of adsorption and q_{max} are higher in the lower pH than the higher pH. As earlier reports of humic acids, the material from laterite soil always shows the same reaction performance as a sorbent. The results insights the pristine role of the humci acid in soil system to rich fertile environment.

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