

An Innovative Approach to the Extraction of Humic Acid from Cow Dung- A Case Study

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Abstract- Intense utilization of humic substances in agriculture has generated a lot of interest among producers, consumers & regulators for an accurate, reliable & cost effective method to quantify humic acid in raw ores & products. Humic acids are dark coloured fully decomposed remains of plant and animal organic matter. They play a leading role in several chemical, geochemical and geological processes. Humic substances also promote plant growth and improve the organic matter status of soil and soil fertility. Here we present a thoroughly validated method for the extraction of humic acid from dry cow dung powder. The proposed methodology is found to be simple, cost effective, and eco-friendly. The process investigated herein provides a promising solution to many global environmental problems.

Index terms- Humic acid, Extraction Procedure, Ultraviolet-visible spectroscopy

I. INTRODUCTION

Humic substances (HS) the most ubiquitous natural organic materials present in soils, sediments and water as a product of the chemical and biological transformation of animal and plant residues [1].

Humic substances are yellow to black in colour with a wide range of molecular weights. Humic substances serve as substrate for microorganism growth on the other hand they have very strong chelate ability with many heavy metals and organic pollutants, which make these toxins more difficult to be removed. As a result of which HS strongly influence the environmental fate of hydrophobic organic chemicals in soils and sediments. Humic substances have a profound influence on the biogeochemical cycles of both natural and anthropogenic constituents [2].

Based on the solubility of humic substances in aqueous solution, these are operationally divided into three different fractions: (i) Humic acid (HA), the

fraction soluble at alkaline pH values; (ii) Fulvic acid (FA), the fraction soluble at all pH values; and (iii) Humin, the fraction insoluble at all pH values with the average properties and structure of a large assembly of components of diverse structure and molecular weight [3].

Humic acid is the fraction of humic substance which is insoluble in water under acidic condition (pH < 2) and is a poly-disperse macromolecule comprising of amino acids, amino sugars, peptides and aliphatic compounds etc. Humic acid is being employed in varied facets veterinary medicine, in agriculture, industries, environment, and even in medicine. HA is known to play a vital role as a chemotherapeutic agent and exhibits anti-viral, anti-microbial, anti-inflammatory, and anticoagulant properties.

A derivative of HA has potent HIV-1 3 and Herpes inhibiting properties. HA impounds on anthropogenic organic compounds, photosensitizes chemical reactions. HA also complexes with heavy metals as well as with carcinogens.

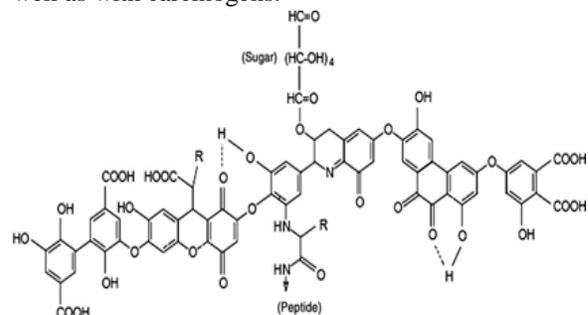


Fig-1 (Model structure of humic acid according to Stevenson-4)

Humic acid originates mostly in the abiotic niche of the lithosphere and hydrosphere due to the humification of biodegradable entities. Parameters to which humification is highly sensitive are pH, temperature, and climatic conditions. In case of any difference in geographical origin, some degrees of

differences are observed in the physical and structural properties of HUMIC ACID, [5] for example marine or river contains a very low percentage of humic acid, abundant undesirable micro flora, and water pollutants.

In addition, the pre and post-process for the concentration of the raw material is time consuming and requires a higher degree of purification. This leads to the generation of many undesirable chemical steps, adding to the cost of the actual extraction process as well as questioning the statutory norms for environmental safety.

In the present work, we have achieved a novel approach for the extraction of humic acid from dry cow dung powder. The process is cost and energy efficient due to renewable and freely available feed stock, Simple reagents are used at room temperature and ambient pressure. In addition, no catalyst or auxiliary substance of any kind is used throughout the process of extraction. The process of purification of raw material in the present work is simpler and easier compared to those which are currently utilized by other synthetic sources. After separating humic acid from dry cow dung powder, the remaining residue left is enriched with humin, and other inorganic and organic complex substances that also have useful properties. Thus the entire process is easily carried out at the laboratory scale as the extraction process is very simple with no risk of accidents.

The main aims of the present study were to (1) develop methodology for extraction of humic substances from cow Manure, (2) characterise humic fractions, (3) elemental analysis of humic acid or analysis of the absorption spectra of HA through UV-Visible spectrometer.

II. BACKGROUND STUDY

There have been several works by various investigators on extraction and characterization of humic acid from different specimens.

Fabiana de Souza et al. [6] presented an approach where subbituminous coal was employed as raw material for the extraction of humic acid (HA) which is to be applied as ceramic dispersant. HA is a good dispersant for the ceramic industry according to the results of the rheological investigation in an alumina suspension. The results shown that the alkaline range

(pH 10–11) is ideal for humic acid utilization as dispersant due to a higher zeta potential and a lower turbidity.

T. Anzai et al. [7] had prepared the rice hull magnetic activated carbon and studied the adsorption property for humic acid from water and high-gradient magnetic separation characteristics. Rice hull was impregnated with an iron nitrate solution and heat treatment was performed in both nitrogen and carbon dioxide atmosphere. In these processes, the rice hull was changed to activated carbon which had a lot of mesopores and nano size magnetite inside of it. Magnetization of RH-MAC increased with an enhancement of iron nitrate concentration during the process.

Seunghun Kang et al. [8] had presented a method where humic acid was obtained progressively extraction from a soil, eight times with 0.1 MNa₄P₂O₇ and two times with 0.1MNaOH solution. The resultant was separated into two humin fractions by their organic carbon contents. The chemical and structural heterogeneity of the humic acids and humins were characterized by elemental analysis, ultraviolet-visible spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy, and solid-state ¹³C NMR

Adrie Veeken et al.[9] had studied the changes in amount and characteristics of humic acids (HA) during the composting of a biowaste in an 80 l composting device. The humic acid was extracted by NaOH, then was purified with HCl-HF and dialyzed. The dried humic acid was then characterised by UV-285, elemental analysis, ¹³C NMR and pyrolysis-GC/MS.

III. EXPERIMENTAL SECTION

Material

In the extraction process the dry cow dung powder is used as a HAs source throughout this study was taken from horizon. Cow dung is a bio-organic, polymorphic fecal residue of the bovine species. It is basically a digested residue of herbivorous matter which is acted upon by symbiotic bacteria residing within the animal's rumen. Hence, finished product is enriched in minerals, carbohydrates, fats, proteins, enzymes, bile pigments, many aliphatic as well as aromatic species and "Humic acid". Since it is biodegradable in nature, dry cow dung powder is non-hazardous. The dried form is the result of the

humification process, enhancing the concentration of humic acid in it.

Humic Acid Extraction

a. Pre-treatment

The humic acid fractions were extracted from the dry cow dung powder. Initially the dry cow dung powder was mixed with distilled water and then stirred for around 20 minutes at room temperature. The process was done for the removal of hay and other light non-humic particles by the process decantation. After removal of the non-humic particles from the dry cow dung powder, slurry thus obtained which was then treated with 0.1M NaOH and stirred for 12hour. The entire was stirred for 12h with 0.1 M NaOH. The entire mixture was allowed to settle before going for the filtration process.

b. Humic Acid Components Separation & Preparation

The solid residue obtained after the filtration process contains humins, ulmic acid, and insoluble bio-organic matter where as the filtrate contained soluble such as Humic Acid, Fulvic Acid, and other biological matter. As we know the residue humic acid is insoluble at low pH, therefore for the precipitation of humic acid the supernatant was acidified by adding 6N HCl at room temperature. The HCl was added slowly with constant stirring in order to minimize the heat neutralization. Supernatant was acidified to pH 1 with concentrated HCl after which the it was centrifuged. The Humic acid precipitates from all alkali extracts were collected after centrifuge. It contains other organic acids, along with FA which remains in solution after the removal of HA by acidification. The humic acid obtained was then washed with double distilled water. It was then left for drying in hot air oven at 373 K.

c. Spectroscopic Characterization of Humic Acid

UV-Visible (UV-Vis) spectroscopy is another technique which can provide useful information on the composition. The visible absorption spectra of extracted humic acid samples were recorded. For the identification and characterization of extracted compound, the resultant compound was mixed with alkaline compound. Visible spectrophotometric measurements were made between 350 and 650 nm.

IV. RESULT ANALYSIS

The absorption value of the extracted humic acid shown in Table. 1. The below graph indicate that light absorption of humic acid is small at the longer wavelengths and increases toward the shorter ones. There exists no distinct absorption band in all wavelengths.

Characterization of Humic Acid by Visible Spectroscopy	
Wavelengths (nm)	Absorbance (a.u)
350	0.787
380	0.633
410	0.482
450	0.326
500	0.216
550	0.154
600	0.112
650	0.094

Table no. 1(Characterization of Humic Acid by Visible Spectroscopy)

The absorption curves of the extracted humic acid shown in Fig. 2.

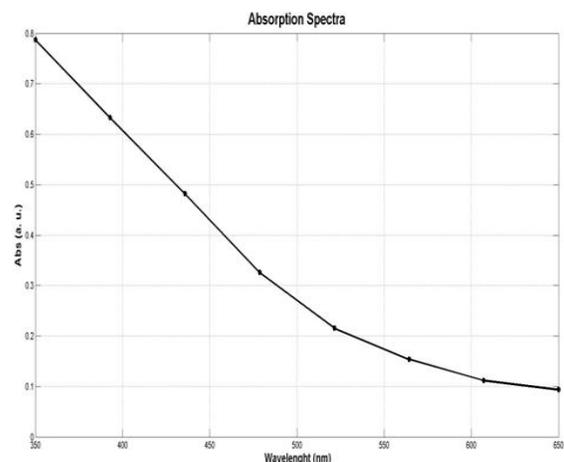


Fig-2 (Absorption spectra of humic acid)

The absorption rate are rather featureless and the increase in intensity of the absorption values is almost consistently from 650 to 350 nm. The absorbance in the visible region, on the other hand, is more complicated to explain, although some authors have suggested that it could principally be related to extended conjugation in aliphatic or polyaromatic structures, quinoide structures and ketoneol-systems, as well as to the presence of metal complexes and/or inter-, or intra-molecular donor-acceptor complexes [10-13]. The spectra of standard HA shows a sharp

narrow absorption band at 350–450 cm indicating presence of heavy metals.

V. CONCLUSION

We have developed a simple, efficient, and eco-friendly method for the extraction of humic acid from dry cow dung powder. The presence of humic acid in the “Dry cow dung” has been investigated and is further confirmed by comparing and analysing spectral data. The results for the characterization of the humic acid sample using UV-Visible spectroscopy is basically in agreement with standard data. This study confirms the efficiency and applicability of cow dung, to be used as a raw material for the extraction of HA. HA can be extracted practically in any laboratory with basic infrastructure, employing simple and low cost process. By using a local organic material with high availability and low cost, humic Acid can be obtained in the form of powder. Hence developed methodology for the extraction of humic acid is a natural boon and will surely give impetus to Green Chemistry.

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