# COATING OF ZnO NANOPARTICLES WITH HUMIC ACID FOR EFFICIENT REMOVAL OF TOXIC METALS FROM INDUSTRIAL WASTE WATER

**Muhammad Zulqarnain[1], Ahsan[2], Numra Shehzadi[3], Abdullah Bin Tariq[2], Muhammad Suleman[2], Komal Sana[2*]**

[1]Department of Chemistry, University of Education Lahore, D.G Khan Campus, Pakistan

[2]Department of Chemistry, Riphah International University Faisalabad, Pakistan

[3]Atta Ur Rahman School of Applied Biosciences, National University of Science and Technology, Pakistan

## Abstract

Humic acid and ZnO nanoparticles were prepared from HA and ZnO by a paralysis method and characterized. The adsorption of toxic heavy metals, Hg(II), Pb(II), Cd(II), Ni(II), and Cu(II) was studied using synthetic solutions and was reported elsewhere. The adsorption of toxic heavy metals from industrial wastewaters onto the surface of Humic acid coated with ZnO nanoparticles was studied here. The percent adsorption increased with increase in pH from 4 to 6 and remained constant up to 10. As HA and ZnO are commonly available at economical price in market, the resulting Humic acid ZnO nano particles is expected to be an economical product for the removal of toxic heavy metals from industrial waste waters. Polluted water containing contaminants adversely affects its PH value, creating it inappropriate for use. Inorganic substances such as solvents, heavy metals, metal ions, and ammonia rear gases and proteins, organic debris, plant material, food, nitrate, and a variety of other contaminants are hazards substances that contaminate the water in shallow and overwater. The current study deals with the removal of heavy metals from polluted water using the process of bio sorption. ZnO nanoparticles-humid acid hybrid was used as an adsorbent for the removal of nickel (Ni) from the industrial wastewater. The synthesized adsorbent was characterized by FT-IR (Fourier Transform Infrared Spectroscopy), UV/VIS spectroscopy techniques. During this study effect of adsorbent dose, pH, initial metal ion concentration, contact time and temperature were investigated to obtain optimum conditions.

**Keywords:** Nanoparticles, Humic Acid, Adsorption, Bio sorption, Waste water

# INTRODUCTION

Water makes up two thirds of the earth's surface and is a necessity for all species. It is detrimental to the entire environment because it has variable physical, chemical, or biological properties after being combined with various organic or inorganic materials, pathogens, heavy metals, or other pollutants [1]. Furthermore, water on Earth is a valuable and limited resource that is endlessly recycled in the water cycle. As a result of the growing contamination of water resources with various organic and inorganic pollutants discharged alongside urban wastewaters, including industrial wastewaters, sustainable management of water resources is urgently needed [2]. Numerous pathogenic organisms found in wastewater, including bacteria, viruses, protozoans, and helminths, are closely linked to serious illnesses like hepatitis A, campylobacteriosis, and leptospirosis. Today, various methods, including UV and chlorination, are used to treat water [3-4].

In the relatively recent area of science known as nanotechnology, methods, patterns, and items with at least one nanoscale dimension are included. This size gives the substance new properties, and their reactivity is greatly enhanced. Reactivity adsorption and an increase in surface area are the novel features at play [5].

Numerous sectors, including the chemical, textile, tannery, plastics, mining, paper and pulp, etc., as well as the chemical industry all release heavy metals into the environment [6]. Human wellbeing is severely harmed by water pollution. Many illnesses, including cholera, diarrhea, typhoid, hepatitis, skin infections, etc., are brought on by drinking this contaminated water or coming into touch with it. In order to stop diseases brought on by heavy metal poisoning, water must be cleaned. The traditional approaches to removing heavy metals include a variety of processes like methylene blue Rane filtering, ion exchange, chemical precipitation, reverse osmosis, reduction, chelation, solvent extraction, electroplating, and evaporation [7].

Typically, substances that have a density of more than 5 grams per cubic centimeter are considered to be heavy metals [8]. They are not compostable and may assemble inside of the body [9]. To name a few industries that contribute heavy metals to the aquatic environment: agriculture, electroplating, corroded underground pipelines, methylene bluestone, business activities like leather-based tanning, sewage, vehicle methylene bluestone, and smelting. The discharge of heavy metal-containing effluents (metals with a specific weight higher than 5g/cm3)

from industries is a global issue [10]. Heavy metals include $Fe^{+2}$, $Cu^{+2}$, $Cr^{+3}$, $Ni^{+2}$, $Co^{+2}$, $Cd^{+2}$, $Zn^{+2}$, etc.

The primary sources of heavy metals are mining, agricultural wastewater discharge, electroplating, battery production, alloy formation, smelting, mineral processing, industrial plant refuse, paint, pigment, and plastic production, among other things. Majority of the metal ions that are released into the environment after use at various locations are substantial amounts and are not always properly clarified [11].

Adsorption is the most efficient method for removing heavy metals from water bodies out of all the various methods available. We can do this to move pollutants, heavy metals, or other impurities from one area to another. It is the procedure that has undergone years of intensive study for the removal of metals from sewage water. Many different kinds of biomaterial, including crab shells, plant matter, fruit pods, eggshells, chitin, chitosan, nutshells, agriculture wastes, fish scales, etc. have been used as adsorbents [16].

## MATERIALS AND METHODS

The methodology used includes a number of stages that are broken down into producing ZnO nanoparticles in humic acid. With a combination of a few physical processes like shaking and centrifuging, this technique primarily uses chemical processes.

**Chemicals**

Zinc Chloride, Sodium hydroxide (NaOH), Distilled water, Hydrochloric acid (HCl)

**Preparation of Humic Acid**

The first step is to produce humic acid in order to make humic acid-ZnO nanoparticles. Biological properties of soil are enhanced by humic acid, a component of humus and a natural component of soil.

From the specifically imported soil from Khairpur, humic acid has been isolated. To create fine, lump-free powdered soil and eliminate larger impurities, the soil was crushed using crushers and sieved through a 100-micron sieve. With 0.1% sodium hydroxide, the powdered dirt was cleaned. After that, it spent 24 hours in the same sodium hydroxide 0.1% solution. Since sodium hydroxide would be in the top portion of the beaker and the powdered dirt would be in the bottom, the top portion of the beaker would be decanted. The powdered alkaline earth is next

neutralized with 0.1% hydrochloric acid. To ensure that the dirt and hydrochloric acid suspension is thoroughly mixed, it is further sonicated using an ultrasonic device. The sonication procedure was carried out several times, with each session lasting close to 15 minutes.

After the sonication procedure, the prepared solution is filtered using filter paper with a particle size of almost 100um. The resulting filtrate was marginally clearer than the sonicated suspension but still required further processing to yield pure humic acid; as a result, it was centrifuged. The centrifuging procedures followed called for maintaining a 40°C temperature and a 4500rpm spin. Since almost pure humic acid was produced, the solution collected in centrifuge tubes was discarded and then kept for later use.

**Preparation of ZnO nanoparticles**

In order to create zinc chloride solution, 20 gm $ZnCl_2$ was first combined with 150 ml of purified water and stirred for at least 20 minutes at a temperature of 35 °C. Sodium hydroxide solution was created by weighing 80 gramme NaOH pellets, mixing them with 80 ml of distilled water, and stirring constantly for almost 20 minutes at a temperature of 35 °C. After the two solutions had been thoroughly combined, 100 milliliters of extra ethanol were added, and a precipitation reaction was carried out while being vigorously stirred. To finish the reaction and obtain the gel-like product, the stirring was restarted for almost 90 minutes. The gel was then dried at a nighttime temperature of 80 °C and then calcined for 4 hours at a temperature of 250 °C in an oven. The preparation of ZnO nanocrystals was the outcome.

**Preparation of ZnO nanoparticles- humic acid hybrid**

To make a solution with 0.1M sodium hydroxide, already made humic acid was placed in a beaker and used as a solvent. Hydrochloric acid 0.1M is added in excess in order to strictly keep the solution's PH level at 5. A shaking container containing 500 mg of pre-prepared ZnO nanoparticle powder and 1 liter of humic acid was placed in the shaker for nearly two days. There was a pause after vigorous shaking. The centrifuge procedure used for this suspension was 3500 rpm(s) for 30 minutes. The substance collected at the bottom of the centrifuge tube is then desiccated at room temperature. The limps are then ground and stored in plastic sacks.

# RESULTS AND DISCUSSION

## FTIR Analysis

A broad spectral range's worth of high-resolution spectral data are simultaneously collected by an FTIR spectrometer. This offers a sizable benefit over a dispersive spectrometer, which measures infrared emissions or adsorption of solid, liquid, or gas. After getting a fundamental grasp of infrared theory, we will look at the outcomes of infrared spectroscopy studies and learn how to analyze the structural information found in the infrared spectra.
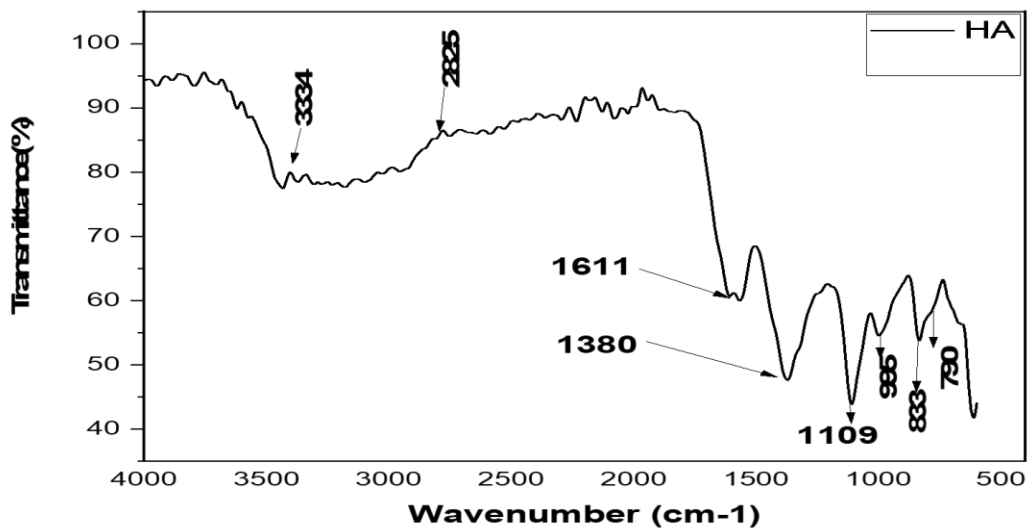


**Figure 1:** FTIR Spectra of Humic Acid

The FT-IR peak that denotes the presence of a -OH group is in the 3300-3400 cm$^{-1}$ region, with a strong, intense peak at 3334 cm$^{-1}$ signifying humic acid. Stretching of the -CH is indicated at 2825 cm$^{-1}$. The values of the -C=0 group lie within the range of 1611 cm$^{-1}$. At a range of 1109 cm$^{1}$, the C-O functional group was visible and -OH displacement is indicated at 995 cm$^{-1}$.
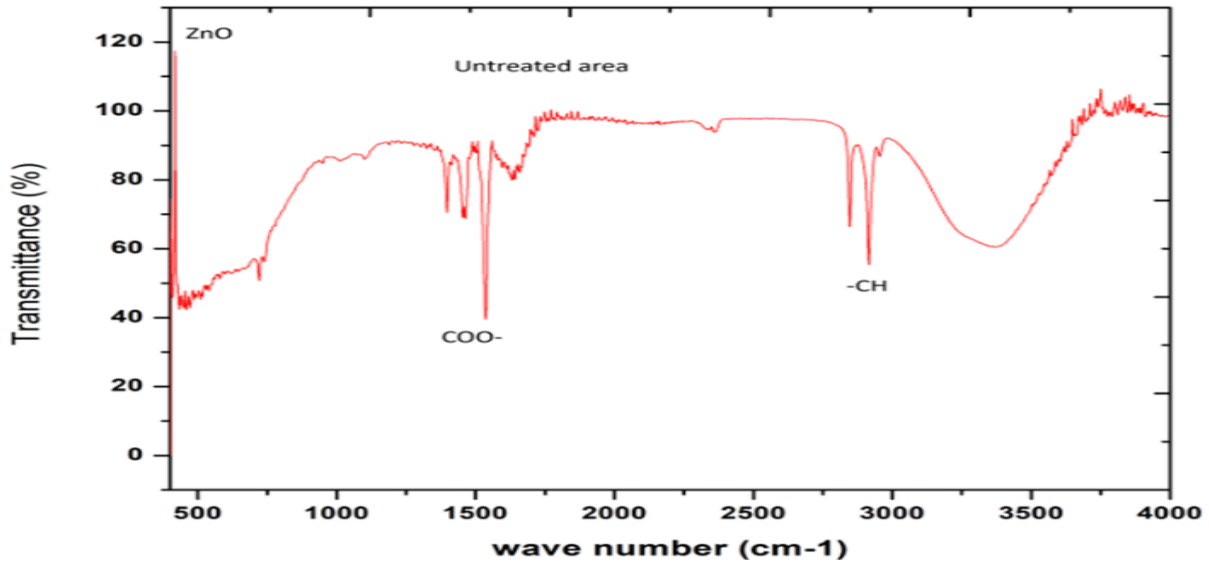
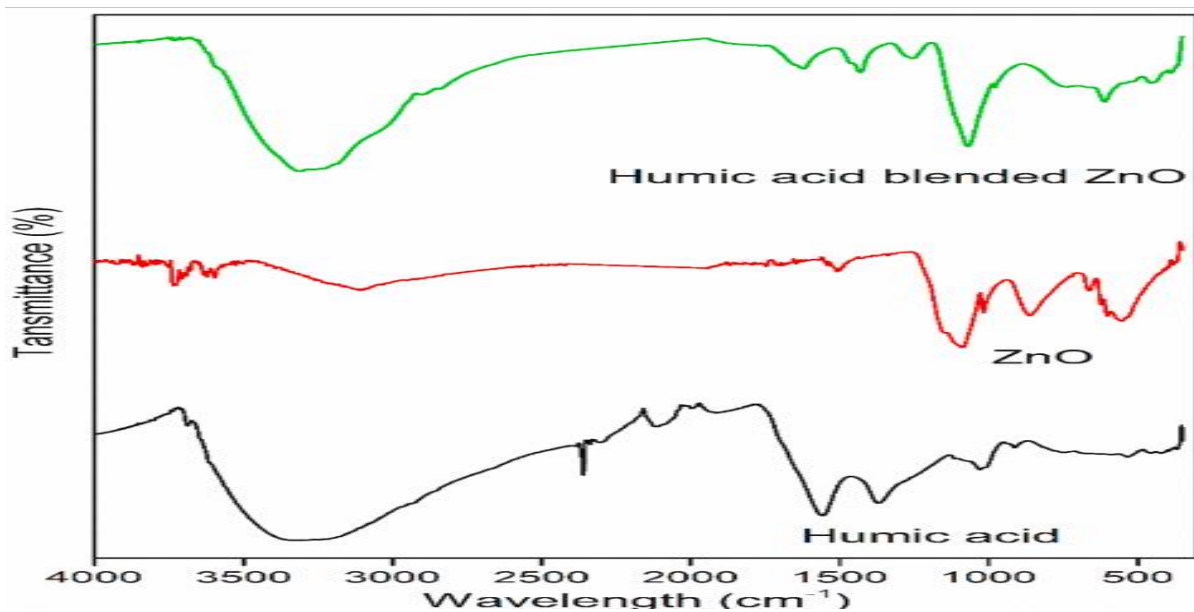**Figure 2:** FT-IR Spectra of ZnO nanoparticles



**Figure 3:** FT -IR spectra of  humic acids blended ZnO    nanoparticles.

ZnO nanoparticles typically exhibit a peak between 400 and 500 cm$^{-1}$. Given that it is located at 572 cm$^{-1}$, the peak above indicates the existence of ZnO nanoparticles. It is thus demonstrated that the procedure for making ZnO nanoparticles is the right one. The nanoparticles it creates are of high quality.

## UV-Visible Analysi

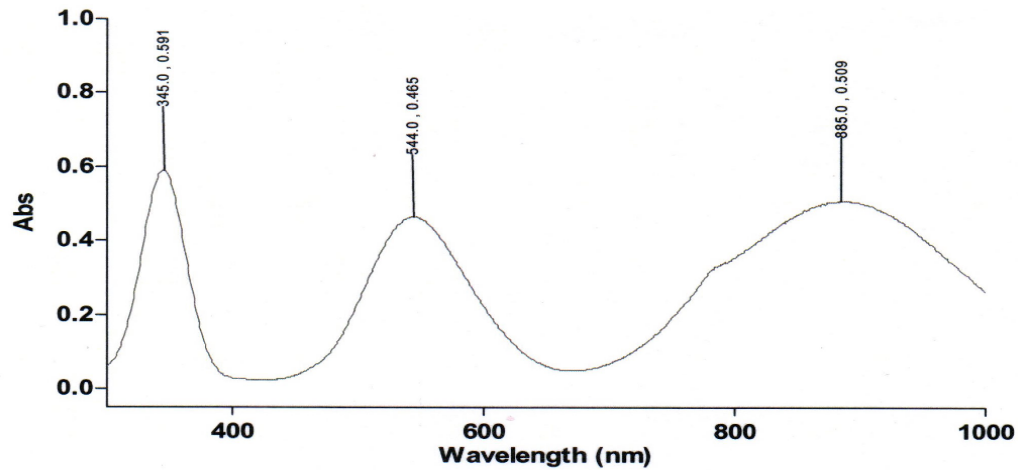The UV-VIS spectroscopy's findings are listed below.



**Figure 4:** UV Visible Spectroscopic Graph

The peak at 345.059nm shows the presence of nickel in the industrial waste.Other peaks show that the industrial sewage water contains other polluting substances.

Absorption spectra of nickel solutions with concentrations ranging from 20 ppm to 100 ppm is given below. The nickel peak was indicated around the concept that the higher the concentration, the higher the peak of the solution. the sharpest point was visible in 100 ppm solution.
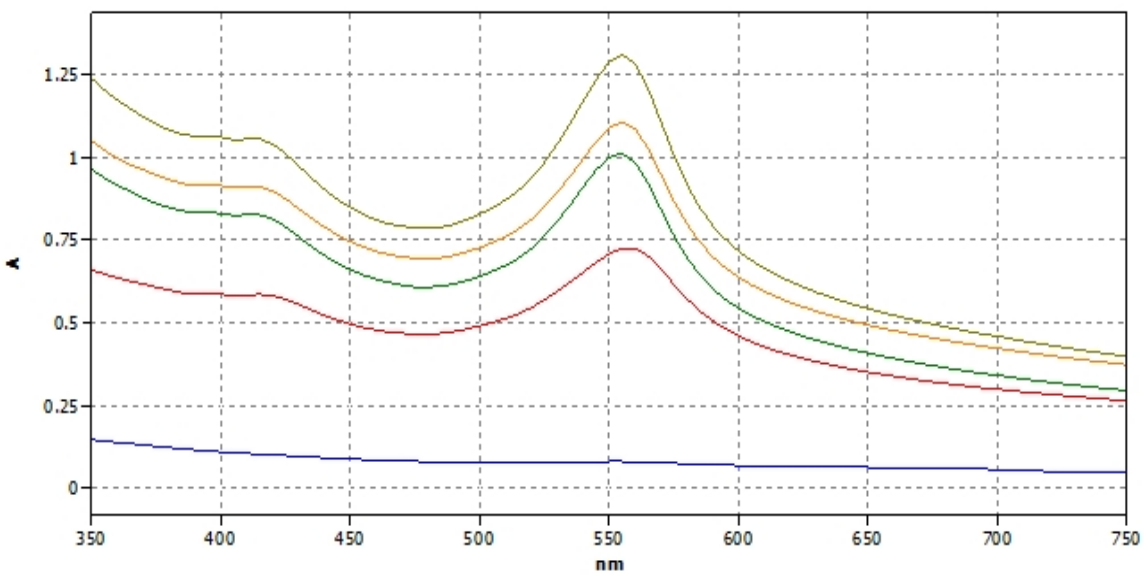
**Figure 5:** Maximum adsorption spectra

The next step was to adsorb the hybrid on the 80 ppm solution, and different concentrations of hybrid were used. The greater the absorbance on nickel, the more pronounced would be the peak, so according to the following graph, the greatest adsorption was noted at 0.02g concentration of hybrid because the peak was the most pronounced or blunt for nickel at this concentration.
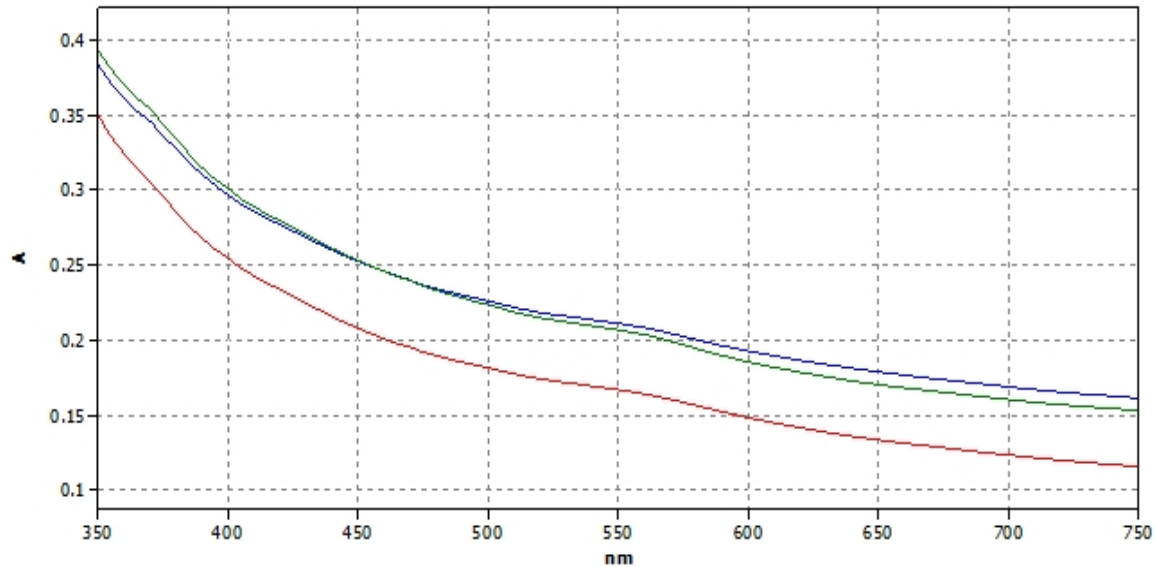


**Figure 6:** Adsorption pattern

Calculation of the % adsorption of the hybrid on the nickel in the solution can be as following

% Absorbance at 0.020 gm

$\{(c_i - c_f)/c_f\}*100$

When the values from the graph were consulted the above equation becomes

$\{(0.8270-0.2069)/0.8270\}*100 = 74.98\%$

% Absorbance at 0.030 gm

$\{(0.8270-0.1607)/0.8270\}*100$

The conclusion drawn from this is that the adsorption percentage remains consistent as concentration increases, requiring only 0.02gm of hybrid to remove nickel from a solution containing 100 ppm of nickel.

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