



Adsorption Study of Natural Resource Remove Heavy Metal in Lemon Peel

¹D. Swapna Sundari, ²V. Ramesh Kumar

¹Reserach Scholar, ²Professor

^{1,2,3}(Department of Chemical Engineering, Osmania University, Hyderabad-07)

¹University College of Technology, Hyderabad, India

Abstract: The Batches of the adsorbents from milled Lemon Peel were tested for their ability to bind Cd (II), Zn (II), and Cr (III). The batch experiments demonstrated that the adsorption was affected by the biomass dose, the pH of the solution, and the initial concentration of the metal. Inversely, metal removal efficiency declined with increasing metal concentration. Three adsorption isotherm models (Langmuir, Freundlich, and Dubinin- Radushkevich) were used to assess the equilibrium data. In the case of equilibrium, the Langmuir isotherm model (R21) is the most accurate. Isotherm studies have been used to ascertain the thermodynamic properties of the procedure. The intraparticle diffusion rate constant, pseudo-first order, and second order kinetic properties of adsorption were determined, and the second order kinetic model was used to describe the data. Maximum amounts of heavy metals (q_{max}) adsorbed at equilibrium for Cd (II), Zn (II), and Cr (III) were 17.5, 31.85, and 25.28 mg/g for lemon peel, and 19.6, 26.28, and 27.67 mg/g for Cd (II), Zn (II), and Cr (III), respectively. The solid-support regeneration study also included a desorption experiment. Temperatures between 20 and 60⁰ degrees Celsius were shown to have a noticeable effect on the adsorption capacity. Enthalpy measurements indicated that the adsorption process is endothermic. The adsorbents' surface shape and functionality were studied using scanning electron microscopy and Fourier transform infrared spectroscopy (FTIR), respectively. According to FTIR study, the hydroxyl, carboxyl, and carbonyl groups present in lemon peel aid in the adsorption of metal ions.

Index Terms – Adsorption study, Heavy metals, Isotherms, Kinetics, Thermodynamics, FTIR.

I. INTRODUCTION

The lowland plains of India are where mung bean, a leguminous annual pulse crop, thrives [1]. Waterlogging is a problem, hence irrigation is crucial to production [2]. Proteins, essential amino acids, vitamins, and minerals are all provided. In addition to being rich in folate, it also contains thiamine, iron, magnesium, and a number of other minerals [3]. Mung bean is cultivated in India for its nutritional value; however, its yield and make-up are affected by a wide range of environmental factors. Heavy metal accumulation is one such issue.

All ecosystems include heavy metals. Agricultural, mining, and industrial operations may boost its concentration in soil beyond its naturally occurring levels. Chemical fertilisers used in farming can lead to increased levels of heavy metals in the soil [1]. Heavy metal contamination of water and soil, resulting from waste from such activities, hinders plant and aquatic life growth [2].

According to studies [4,] heavy metals have an important role in plant growth and development. However, many plant/crop advancements and output have been impeded by the excess availability of heavy metals from the environment [5]. Heavy metals accumulate in the body and can cause serious physiological changes. Irritation of the nose, mouth, and eyes, as well as headaches, stomach aches, dizziness, vomiting, and diarrhea, and a higher risk of tubular dysfunction have all been linked to exposure to high concentrations of Cu ions [6]. In addition to damaging adults' kidneys and increasing their blood pressure, Pb ions can stunt children's physical and mental growth [7]. Many of these toxins have been traced back to common food and drink items, herbal remedies, cosmetics, and other commercial products [3].

There are a wide variety of analytical methods used for detecting trace or ultra-trace quantities of heavy metals in materials like plants [8]. As a spectroscopic method, ICP/OES spectrometry (inductively coupled plasma/optical emission spectrometry) can be applied to samples to identify minute amounts of elements. The As, Cu, Zn, Cd, and Pb concentrations in soft drink samples were determined using this method [9]. In particular, four marine fish species were reported to have detectable levels of Cr, Cd, Cu, and Zn in their edible parts [10]. Scanning electron microscopy (SEM) and atomic temperature spectrometry (ATS) are two examples of elemental analysis techniques. SEM has a wide linear dynamic range, high matrix tolerance, multi-element capability, high sensitivity, good reproducibility, low matrix effect, and wide dynamic linear range for analysing rare earth elements (REEs). Major and trace components in plant samples can be analysed using this innovative technique [12]. Accurate and exact results cannot be obtained without proper sample preparation [13]. It takes a long time and requires a lot of effort to carry out several ash treatments, such as the dry and wet ash processes. Sample preparation via microwave digestion is fast and efficient [14].

Rapid industrialisation and current farming practises may contribute to heavy metal deposition in the environment [15]. Chemical and fertiliser use may increase environmental heavy metal deposition [4, 16, 17]. These contaminants are resistant to degradation by soil bacteria and hence remain in the environment for longer, making them available to plants [18].

Higher concentrations of heavy metals in the crop lead to a number of environmental issues, including: a) poor germination and low crop productivity [19], which may alter its nutritional values [5], and b) serious environmental damage to the soil, cropping, vegetation, and ultimately human health [20]. When ingested by humans, it also affects health [21].

Studies have indicated that dumpsite soils contain high levels of heavy metals [18]. Heavy metals may accumulate in irrigation water in Nalgonda as a result of urbanisation and a lacklustre waste management system, which has led to the proliferation of dumpsites (references 5, 22). In addition, the farmers and producers of mung bean leaves have likely employed a wide variety of pesticides, fertilisers, and herbicides, all of which can degrade soil quality and increase exposure to toxic heavy metals. It is crucial to thoroughly measure metal concentrations and conduct appropriate management due to their toxicity and detrimental effects on human health and the environment. To reduce exposure to hazardous heavy metals, it is essential to keep tabs on moonbeam's heavy metal levels. The present investigation employed SEM and ATS for this purpose.

Figure 1.1: Vigna Radiata leaf's

II. BATCH STUDIES

For the batch testing, 100 ml of metal solution was added to a 250 ml flask. After adding adsorbent (0.1g) to a solution of a predetermined concentration, the flasks are shaken at 200 rpm in a temperature-controlled incubator. Used fluids included anywhere from 10 to 100 mg/l of metal ions. In the batch experiments, the pH of the solution was maintained at 5.50.5 for a contact time of 120 minutes. By adding HCl or NaOH to metal solutions, scientists were able to study the effects of a wide pH range (from 2 to 7). To determine whether or not the samples included metal ions, they were filtered to remove any remaining particles and then put through an atomic absorption spectrophotometer. Adsorbent dose, contact time, initial concentration, pH, adsorption rate, equilibrium constant, and other factors all had a role in the results. The thermodynamic parameters and adsorption isotherm models were investigated to gain a deeper comprehension of the adsorption behaviour.

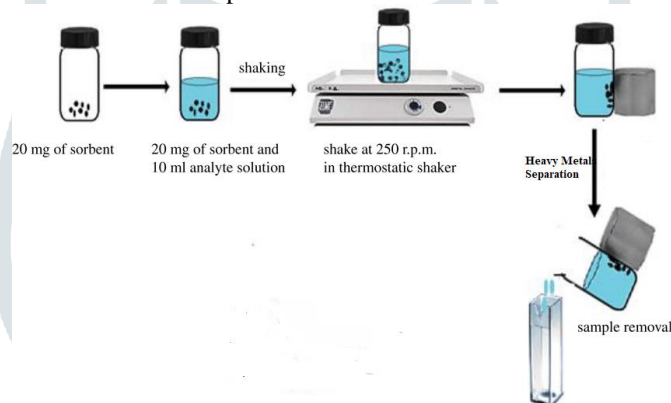


Figure 1.3 Batch shaker Studies

III. METHODOLOGY

Sample collection and study area description

The study were conducted by chemical dept researcher, at Hyderabad's Osmania University. Mung bean seeds were collected at random from farmers in Nalgonda, around 220 kilometres north of Hyderabad. This crop was selected because of its contribution to pollution in the study area as a result of its massive production, consumption, and improper waste management [23].

Instruments, reagents, and chemicals

Equipment used includes an electronic scale, muffle furnace, pH metre, conductivity metre, scanning electron microscope with Fourier transform infrared spectroscopy, air-circulating oven, and test tubes. In order to calibrate an ATS metre, standard solutions of Cu, Cr, and Zinc (1000 mg/L, Certipur® Single-Element Standard for SEM-FTIR) were procured and subsequently diluted. Nitric acid (HNO₃), hydrochloric acid (HCl), and perchloric acid (HClO₄), all at 70% concentration, were ordered for analytical use.

Preparation of the sample

Cleaning procedures included detergent washing, rinsing with distilled water, soaking in 10% HNO₃ solution for 24 hours [24], washing with distilled water, and drying in a drying oven at 105 °C for 5 hours for all glassware, containers, crucibles, mortars, and pestles.

Before being dried in the air, the mung bean seeds were washed multiple times with distilled water to remove any remaining dirt. The dried bean was pulverised into a powder using a porcelain mortar and pestle, then passed through a 2.0 mm sieve before being stored in a zip lock bag at room temperature.

Digestive digestion of samples

Using a muffle furnace, we dry-ashed 5.0 g of ground moonbeam leaf's powder by gradually raising the temperature to 550 °C and leaving it there to ash for 6 hours. The crucibles were labelled in triplicate with the sample number. After removing the sample from the oven, cooling time was given. The ash was moistened with water, then 2.5 mL of concentrated HNO₃ was added. The crucible was placed on the hot plate, and the glass was used as a timepiece. The digestion took place at temperatures between 90 and 95 °C for 60 minutes. The ash was digested once more on a hot plate until the white vapours vanished and the sample volume reached 2 mL, after which it was dissolved in 5 mL of 9.25% HCl. The mixture was cooled and filtered before being supplemented with 20 mL of distilled water. Before being stored at 4 °C for analysis, the filtered sample was diluted to the 50 mL mark on a standard volumetric flask. Blanks were produced [20], [22], and [25] to check for cross-contamination from the chemicals.

Standard solution preparation

Standard solutions (Table 2) for each metal were prepared from the stock solution (1000 mg/L). To prepare 10 mg/L concentration working solutions, 1 mL of 1000 mg/L stock solution was pipetted into 1000 mL volumetric flasks, and the contents were diluted to the mark using deionized water. Using the metal's linear response range as a guide, working solutions of 10 mg/L were diluted to generate 0.1-2.8 mg/L [14] calibration standards. The elements were then calculated using an ICP-OES that had been blank- and standard-solution-series-calibrated. Using the procedures detailed in [18], calibration curves were generated for each component. This method achieves a high degree of precision and accuracy in multi-elemental analysis by combining a high sample throughput with outstanding sensitivity. Standard deviation (SD) was used to quantify the consistency with which experimental results were obtained from actual samples to determine the analytical method's precision. Accuracy was verified through calibration (with reference solutions).

pH of the soil conductivity

Mung bean leaf's soil was sampled using a professional soil sampling procedure, with a polyethylene tube inserted to a depth of around 40 cm. pH and electrical conductivity of the soil were measured using the technique described in [26]. Sample pH was measured using a portable Hanna pH metre according to the protocol described in [27]. To a beaker containing 50 cm³, 20 g of dry soil was added, along with 20 cm³ of distilled water. For thirty minutes, the liquid was stirred with a glass rod and then put away. A pH metre that had previously been calibrated was used to determine the slurry's pH level. In order to calculate electrical conductivity (EC), a modified method similar to that described in [27] was utilised. A 25 gramme sample of air-dried soil was placed in a 250 cm³ beaker, and distilled water was slowly poured over the top in a uniform pattern until the soil seemed wet. A consistent soil paste was made using a stainless steel spatula. After that, 50 cm³ of distilled water was added to the beaker, and it was stirred for 1 hour while covered with a Petri dish. To measure the soil's electrical conductivity, we poured 40 cm³ of the diluted extract into a 100 cm³ beaker and inserted the conductivity metre electrode.

Table 1 Determination of heavy metal using SEM-FTIR ATS from Vigna Radiate leaves and Bean

Parameters and Instruments	Operating Conditions
Applied Frequency Power (kW)	1.3
Viewing mode of Plasma	Co-Axial
Flow rate of plasma (L min ⁻¹)	14
Flow rate Auxiliary (L min ⁻¹)	1.5
Pump Speed	16
Time of Integration	7

IV. RESULTS AND DISCUSSION

pH and electric conductivity

Based on the data, we know that the soil sample had a pH of 6.93 0.153 and an electrical conductivity of 0.18133 dS/m 2.52). If the pH of a soil sample is below 6.5, we classify it as acidic; if it's between 6.5-7.8, we call it neutral; and if it's over 7.8, we call it alkaline. Soil samples are classified as either normal or abnormal based on their electrical conductivity. Below 0.8 dS/m, between 0.8 and 1.6 dS/m for salt-sensitive plants, between 1.6 and 2.5 dS/m for salt-tolerant plants, and beyond 2.5 dS/m for most plants is harmful. The pH of the soil sample was determined to be 6.93 0.153 through experimental analysis, indicating that the soil was normal (middle), weakly acidic, and suitable for mungbean production. Soil with a pH of 6.2–7.3, specifically loam or semisandy soil, is optimal for growing this plant. The soil sample pH measured in the lab was 6.93, therefore it was within the acceptable limit. The soil sample's electrical conductivity was found to be 0.18133 dS/m 2.52) based on experimental measurements. The findings showed that the soil sample's EC was within the typical range (0.8 dS/m), indicating that the soil was healthy.

Instrument calibration

The SEM-FTIR ATS Method was calibrated using reference solutions with known concentrations of all metals. Each metal's working standard solution was freshly made by diluting the intermediate standard solution to the proper concentration. Table 2 displays the values of the correlation coefficients of the calibration graph as well as the concentrations of the intermediate standards and working standard solutions for each metal.

Table 2 Solutions and Correlation coefficient of concentration

Metals	Intermediate Concentration (mg/L)	Calibration graph	Standards Concentrations (mg/L)
Cu	20	0.99767	0,0.029,0.058,0.089,0.29,0.59,0.85,1.13,1.6
Cr	20	0.999455	0,0.25,0.41,0.85,1.25,1.8,2.5,3.1,3.6
Zn	20	0.999978	0,0.003,0.0056,0.085,0.29,0.58,0.87,1.4,1.5

Detection Limit of an Analytical Method

An analytical method's detection limit is defined as the lowest concentration of an analyte for which a 99% confidence interval exists [27]. Also, the standard deviation of the blank emittance multiplied by a constant yields the limit of detection (LOD), which is the smallest quantity of analyte that can be separated from stochastic variations in a blank. The mass of the analyte that produces a signal equal to three times the standard deviation of the blank is typically used to establish the limit of detection [27]. The study's detection limit was determined by determining the standard deviation of seven blank signals, with each signal being measured three times to ensure accuracy. Table 3 displays the results of the LOD calculations performed on the mung bean samples. Using the formula, we can get the formula detection limit for each element.

The LOD is set at three times the standard deviation (SD) of the blank [27]

The minimum quantifiable level (MQL) is defined as the concentration of analyte in a sample matrix that yields a signal at least 10 times larger than the standard deviation of the blank. The formula is as follows:

Upper bound on quantification = 10x The blank standard deviation [27]

The MQL is higher than the detection limit of the instrument, proving both the availability of the method and the superior detection of the heavy metal content in the sample by the instrument [28]. The lowest MQL value possible is indicative of a high degree of accuracy. This meant that the procedure (method) could be relied upon more often.

Table 3 Limits of Cr, Cu, Zn metals in Vigna radiata leaf's bean

Metals	MDL in mg/L+SD	MQL in mg/L+SD
Cu	0.118	0.37
Cr	0.446	1.25
Zn	0.55	1.6

Analytical technique evaluation

The proposed approach was applied to both non-spiked and spiked samples of mung bean, and the results were determined in triplicate. Table 4 displays that mung bean recovery percentages for the tested metal ranged from 96.5% to 110.5%. Validity of the suggested approach for mung bean analysis was confirmed by results of recovery tests for the samples falling within the permitted range. These results were within the expected range of 80 to 120% for the elements, hence the analysis method was quite accurate [32]. The following equation was used in the computation.

$$\text{Percentage recovery} = \frac{\text{Concentration in spiked sample} - \text{Concentration in unspiked sample}}{\text{Amount spiked}} \times 100 \quad [29]$$

Table 4 Percentage recovery of Chromium, Zinc and Cadmium

Heavy Metals	Sample Concentration (mg/L)	Added Amount (mg/L)	Spiked sample (mg/L)	Deviation Standard	% recovery
Copper	8.53	0.6	7.09	0.040	110.5
Chromium	0.33	0.5	0.91	0.324	105.22
Zinc	2.55	0.5	3.11	0.097	96.5

Heavy metal concentrations in mung beans leaf's

The methods to analysis of SEM-FTIR ATS was used to determine the levels of Zinc, copper, and chromium in mung bean leaves. Figure1 displays the lead, copper, and chromium concentrations in mung bean to be 2.51 0.236, 6.53 0.039, and 0.38 0.085 milligrammes per millilitre, respectively. According to WHO standard (1996), the maximum allowable levels of lead, copper, and chromium are, in order: 2 mg/L 0.236; 6.53 mg/L 0.039; and 1.3 mg/L 0.085. According to the measured Cr, Zn, and Cu concentrations in mung bean seed. The analysis showed that the plant's levels of copper and chromium is below the threshold for human consumption. Toxic musculoskeletal, renal, ocular, neurological, immunological, reproductive, and developmental effects; kidney damage; headache; hearing and speaking difficulties; fatigue and irritability; all may result from lead concentrations that are higher than standards, which reduce plant productivity and put human health at risk [20]–[30]. The local farmers' heavy reliance on dirty irrigation water may be the result of years of accumulated garbage, such as animal corpses. The use of various fertilisers and other agricultural inputs during crop production may also have a role in the accumulation of excessive lead in mung bean seeds [31].

While the sample's copper content was well below the legal limit, it diverges from the results of other studies [32] because Cu concentrations vary depending on soil type and pollution levels. The increased concentration of copper in mung bean seed samples was found to have a plethora of potential causes, including but not limited to the introduction of various waste elements into the irrigation water and the usage of fertilisers by farmers. [20]. Both natural and anthropogenic mechanisms contribute to the formation of chromium. Since chromium uptake by plant shoot is typically modest, it was not discovered in several plant sites, indicating that chromium is not crucial for plant growth [33]. According to the numbers, mungbean seeds had a chromium content that was well below the recommended maximum. Cr, a cofactor of insulin, is useful in the treatment of diabetes when it is present in therapeutically appropriate concentrations. Sorghum, maize, wheat, and barley were all found to have chromium concentrations below the legal limit [20], with values of 0.95, 0.54, 0.43, and 0.29 mg kg⁻¹ [34].

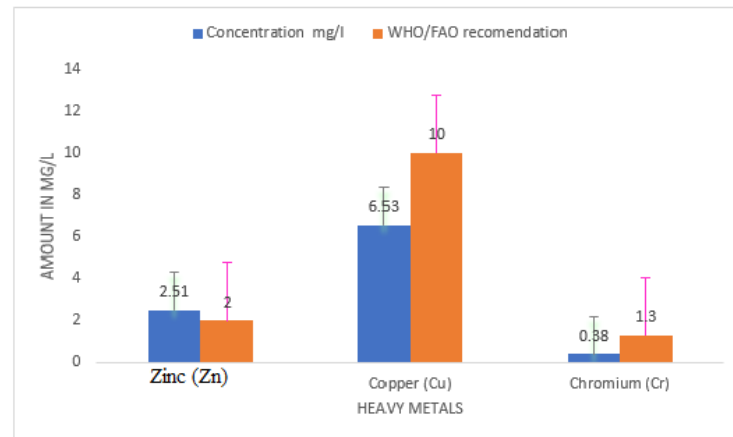


Figure 1.4 Heavy Metals remove percentage from mung bean leaf;s

V. CONCLUSIONS

In this analysis of heavy metals using SEM-FTIR-ATS was used to identify heavy metal buildup (Zn, Cu, and Cr) in irrigated mungbean. The research showed that while the levels of copper and chromium were within safe parameters, the levels of lead were well beyond the threshold recommended by the WHO and should not be consumed. To prevent the accumulation of hazardous heavy metals in food crops, it was required to monitor effluents. As a result, less heavy metal contamination will pose a threat to human health.

In this batch experiment, *Vigna radiata* leaves were employed to remove Zn-(II), Cr-(III), and Cu-(II) from water. The removal efficiency is quite delicate to the working conditions, especially the pH. The kinetic data were best suited by the equations of second order kinetics. G values that are negative indicate that the process is viable and spontaneous. Several equilibrium models, including the Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models, were used to examine and interpret the equilibrium data. Over a wide range of flow rates, breakthrough curves for zinc ion adsorption on *vigna radiata* packed columns were shown. Adams-Bohart and Wolborska's models were used to incorporate the experimental data.

Low-cost technologies for treating inorganic wastewater are becoming attractive as the world moves towards stricter environmental regulations. Heavy metal removal from metal-contaminated wastewater has been studied extensively recently, and numerous low-cost adsorbents have been developed from agricultural waste, industrial by-products, and natural materials. According to a review of 102 papers published between 1984 and 2005, low-cost adsorbents derived from agricultural waste have superior removal capacity to activated carbon (Cr(VI): 170 mg/g of hazelnut shell activated carbon, Ni(II): 158 mg/g of lemon peel, Cu(II): 154.9 mg/g of chemically modified soybean hull, Cd(II): 52.08 mg/g of jackfruit). It's worth noting that the adsorption capabilities of the low-cost adsorbents listed above for various metals can range widely depending on factors like the adsorbent's specific features, the depth of its surface modification, and the concentration of the adsorbate to begin with. When deciding on the best low-cost adsorbent for treating inorganic wastewater, it is important to consider both its technical applicability and its cost-effectiveness.

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