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One-Parameter (Henry's isotherm) Adsorption of Cu^{2+} Cation from Aqueous Solution with Watermelon (Citrullus lanatus) Bio-Sorbent Seeds Powder.

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Abstract: *The application of an agro-based bio sorbent [water melon seed powder (WSP)] in the sorption of copper (II) ions in aqueous solution were established. The sorbent (WSP) was characterized for moisture content (3.04%), point of zero charge (6.00), loss on ignition (65.8), specific gravity (2.13) and FTIR before and after sorption. Henry's one parameter adsorption model with the constant (K_{He}) of 202.03, regression (R^2) of 0.97 was adopted in studying the process favorably. The zero point of charge (ZPC) declared the bio sorbent to be more active under alkaline ($pH \geq 8$) condition or modification. The actual average percent of Cu^{2+} removal was statistically calculated to be (98.01 ± 0.54) % with 1g/50ml (pH >6).WSP has been a low cost, and environmentally renewable bio sorbent has been ascertained to be potentially active naturally in the removal of metallic pollutants like Cu^{2+} in solution.*

Keywords: Watermelon seed powder, copper ions, bio sorbent, henry's isotherm, aqueous solution**.**

1.0 INTRODUCTION

Metals like copper are considered toxic and not biodegradable even at a very low quantity in the environment [1]. Hence, it will be imperative to undertake pragmatic measures in the prevention of high levels of copper ions in water, air and soil media. Copper exists in the liquid and effluent wastes of most manufacturing industries, such as fertilizer, wood preservatives, metal cleaning, plating baths, paper with pulping and refineries [2]. Copper, among the heavy metals, is conceivably hazardous as a result of its natural toxicity and reactions in the soil [3]. The extreme and unconscious ingestion of copper ion usually through the water allows its buildup in the liver with continued inhalation of copper-containing sprays with lung cancer, kidney damage, gastrointestinal problems, anemia and kidney damage [4]. Consequently, it is essential to remove deposits of copper from our potable and drinking water and the wastewater before release into receiving bodies within the environment. Be that as it may, different treatment strategies have been utilized to dispose of or decrease copper in wastewater including precipitation, adsorption on activated carbon and different adsorbents with reverse osmosis and ion exchange [5]. Among these referenced procedures, adsorption is a very potent strategy as a practical and proficient technique that eliminates metallic pollutants from wastewater [6]. Lately, there have been considerations on the application of natural or chemically modified potential agro-based adsorbents for the treatment of wastewater loaded with toxic metals [7]. Therefore, we adopted natural and unmodified watermelon seeds as an alternative low-cost sorbent in the removal of copper ions from aqueous solutions and to evaluate the adsorption performance with one parameter adsorption model of Henry's isotherm which defines adsorption with a direct relationship with the active area of the adsorbate and the fractional pressure of the adsorbent [8]

2.0 MATERIALS AND METHODS

2.1 Analar Grade Cu (II) Nitrate, HCl, NaOH, double distilled water, sieve mesh, mechanical blender, and relevant glass wares.

2.2 Bio-sorbent preparation and characterizations

Watermelon seeds (WS) were acquired and washed more than once with water to dry at daylight in a shade for 48 hours. The dried seeds crushed in a mechanical processor into a fine powder with a size of 225µm. It was preserved in a sealed glass bottle for use as adsorbents.

2.3 Specific gravity

Was determined by the density bottle method [9].

2.4The loss on ignition (LOI)

Was estimated by this method [10].

2.5The Zero point of charge (ZPC)

This was determined with the solid expansion technique [11]

2.6 Sorption process

0.03M stock solution of copper (II) nitrate (5g/L) was prepared in double-distilled deionized water with different serial concentrations as 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5 and 5.5g/50ml. 10g WS powder adsorbent was then added to 50 ml of each percent concentrations in 500ml Erlenmeyer flasks at ambient temperature, 150rpm with orbital shaker for 30minutes accordingly. The amount of Cu (II) adsorbed per unit of WS (mg copper per g WS) was calculated according to the equation below and the residual Cu (II) concentration in the supernatant after adsorption was immediately analyzed with AAS at a wavelength of 312nm[12]. The FTIR spectra of WSP (with and without sorption of copper) were evaluated with the KBr method

2.7 One-Parameter Isotherm (Henry's Isotherms)

This isotherm model depicts a proper fit for the adsorption of adsorbate at moderately low composition such that every adsorbate is isolated from their closest neighbors [13].
Along these lines, the balance adsorbate focuses on the fluid and adsorbed stages are identified with the direct plotting of qe against Ce (Equation 1)

$$q_e = K_{HE} C_e, \quad (1)$$

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

Where qe is the measure of the adsorbate at equilibrium (mg/g), K_{HE} is Henry's adsorption constant, and Ce is the equilibrium concentration on the adsorbent. (Equation 2)
The adsorption limits (% removals) of the adsorbent were calculated according to equation 3 below

$$\text{Percentage of removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (3)$$

3.0 RESULTS AND DISCUSSIONS

Table 1.Physical Parameters of watermelon seed powder

Parameter	Value
Moisture content	3.04%
Point of Zero charge	6.00
Loss on ignition	65.8%
Specific gravity	2.13

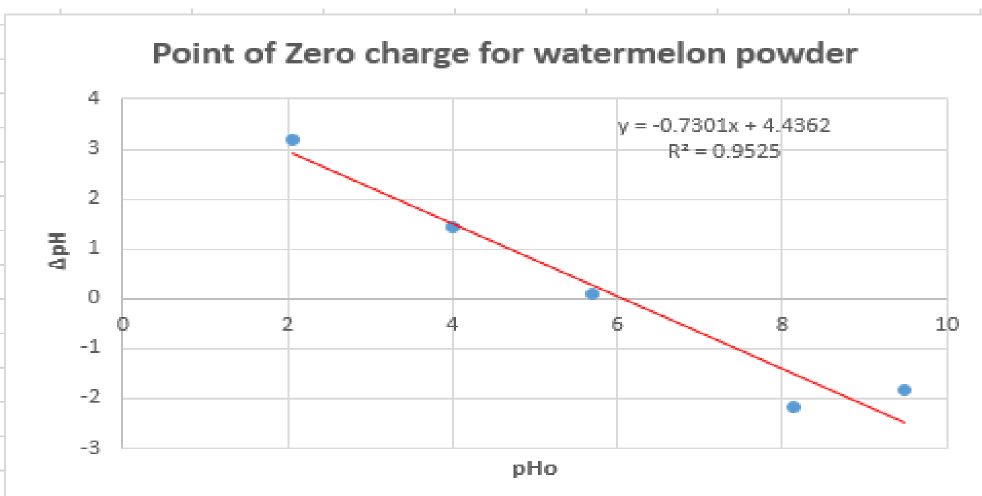

Figure 1. The zero point of charges for watermelon seed powder

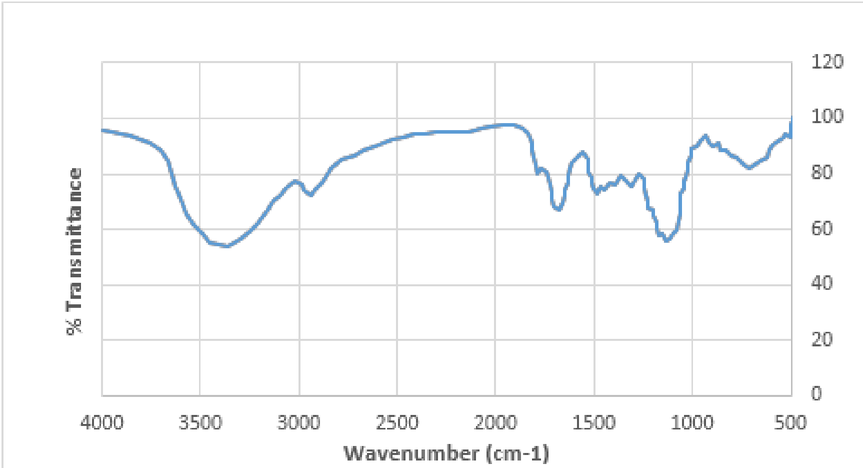

Figure 2. FTIR spectrum of WSP before adsorption

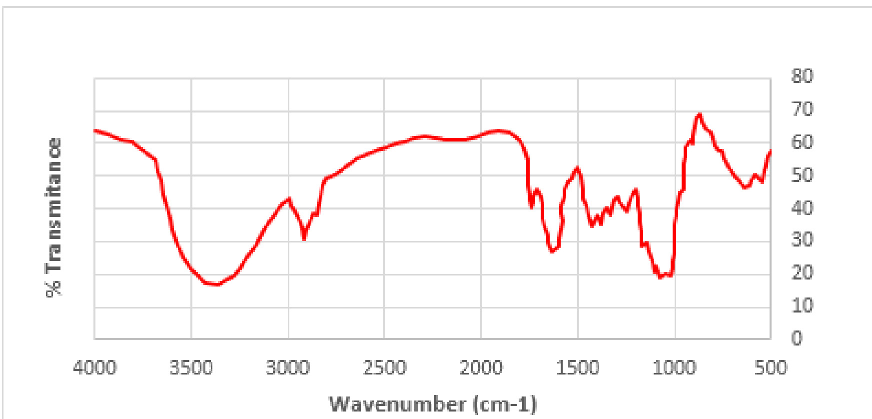

Figure 3. FTIR spectrum of WSP after Cu^{2+} adsorption

Table 2. Henry's Adsorption estimate of Cu^{2+} Sorption by WSP.

C_1 (g/50ml)	C_2 (g/50ml)	qe=[C1-C2]V/M	% Removal	Descriptive Statistics	Values
1.0	0.008	0.430	99.20	Actual Value	98.01 ± 0.54
1.5	0.018	7.410	98.80	Mean	98.01
2.0	0.045	9.775	97.75	Std. Deviation	0.54
2.5	0.005	12.250	98.00	Maximum	99.20
3.0	0.065	14.675	97.83	Minimum	97.57
3.5	0.085	17.075	97.57	Range	1.63
4.0	0.087	19.566	97.83		
4.5	0.098	22.010	97.82		
5.0	0.120	24.400	97.60		
5.5	0.125	26.875	97.73		

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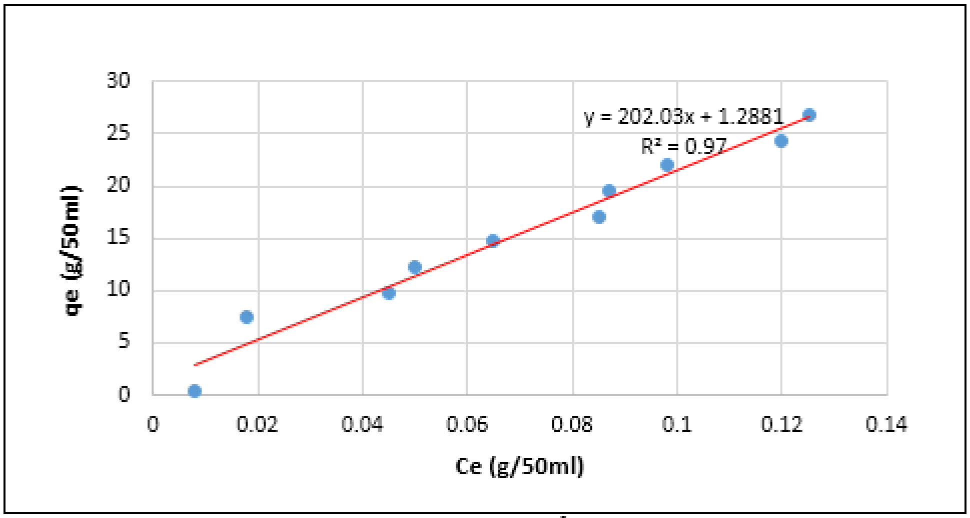

Figure 4. Henry's isotherm for the sorption of Cu^{2+} on natural WSP

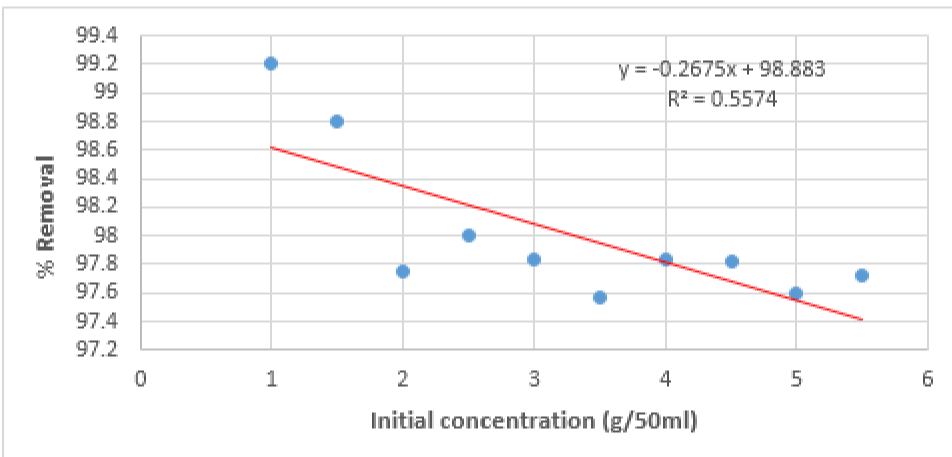

Figure 5. Removal capacities of natural WSP on Cu^{2+} from aqueous solution

Table 1 presents some physical characteristics of the watermelon seed powder as a bio sorbent material. The high level of loss on ignition (Table 1) especially is the indication of active organic material as natural products. The zero point of charge with the intersection at point 6 on the x-axis (Figure 1) implies that pH less of 6 induces the bio sorbent material to be reactive with cationic species while above will be dominated by anionic species or radicals. This supported the fact that lower pH to 6 (acidic) enhances the bio sorbent material with poor affinity with positively charged ions like copper while above 6 (alkaline), the bio sorbent is strongly attached with the cations. The FTIR spectra of the bio sorbent before and after the sorption process (Figures 2 and 3). These identify some functional groups that retain the sorption capacity of metallic pollutants in solution.
The spectrum (Figure 2) shows some peaks that correspond to various functional groups. A band with an intense peak at $3371cm^{-1}$ is to the –OH stretching vibrations from lignocellulose. At $2917cm^{-1}$, the –CH stretching vibrations of methyl and methoxy groups were recorded [14]. Similarly, at $1734cm^{-1}$ is the –C=O stretching of carboxylic acid and esters with symmetric and asymmetric vibrations of ionic carboxylic groups (-COO-) respectively at 1633 and $1423cm^{-1}$[15]. $1383cm^{-1}$ is assigned to symmetric stretching of –COO- of pectin [16], at 1300 to $1000cm^{-1}$ is the stretching vibrations of carboxylic acids and alcohol [17].
Treated WSP (Figure 3) reflects a slight shift from the initial peaks before sorption. At 3371 to $3407cm^{-1}$, 1734 to $1736cm^{-1}$, 1633 to$1621cm^{-1}$, 1423 to $1417cm^{-1}$, 1323 to $1327cm^{-1}$ and 1062 to 1066 cm^{-1} due to copper ions sorption and perhaps with the generation of ions through hydroxyl and carboxylic groups as the components of the watermelon seed.

Table 2 is the henry's adsorption estimate of Cu^{2+} sorption by WSP. The isotherm was achieved maximally at 0.97 regression coefficient and with the constant value (K_{He}) of 202.03 (Figure 4) and percent copper removal (Figure 5) which was a function of higher pH (pH > 6; at 1g/50ml of copper solution)

4.0 CONCLUSION

Watermelon seed powder has been adopted and successfully applied as a bio-sorbent in the treatment and elimination of Cu^{2+} from aqueous solution. Without modification, WSP was discovered to be quite effective as sorbent at higher pH (alkaline) condition with regards to henry's one parameter isotherm model.

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