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Assessment of Effectiveness of Watermelon Rinds on Removing Copper (II) Ions from Synthesized Wastewater

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Abstract

This paper presents results on the investigation of Copper II ions (Cu^{2+}) removal from synthesized wastewater using watermelon rinds, under laboratory scale batch experiments. The effects of pH, contact time, particle size and dosage of the adsorbent on the adsorption of Cu (II) were studied. The concentration of Copper in wastewater was determined by using Atomic Absorption Spectrophotometer (AAS). Results show that the removal mechanism was dominantly adsorption, which is dependent of the physical and chemical characteristics of the adsorbent material. The chemical composition of the adsorbent was analyzed by AAS and was found to compose mainly of essentially nutrients for plant growth and phenolic compounds. The zero point of charge of the watermelon rinds was obtained at a pH of 5.9, optimum pH was 7.9, optimum dosage of watermelon rinds was 0.2 g/50 ml (with an initial Copper concentration of 15.72 mg/l) and the optimum contact time was approximately 120 minutes. The final concentration of Copper at optimum conditions was 0.115 mg/l, which is lower than the recommended limits for municipal and industrial wastewaters of 2.0 mg/l. Adsorption equilibrium was better described by the Freundlich model (0.929) than the Langmuir isotherm model (0.87).

Keywords

Adsorption, Batch, Watermelon Rinds, Wastewater, Copper

1. Introduction

Wastewater may be defined as any water that has been adversely affected in quality by natural or anthropogenic influences [1]. Heavy metal species are some of the most common pollutants that are found in industrial wastewater [2-5]. Heavy metals are natural constituents on the earth, commonly known with properties such as having persistence, high toxicity and also serving as non-biodegradable pollutants when they accumulate in the ecosystem [6]. Previous studies [6-7] have described that heavy metals are applied to the group of metals and metalloids with atomic density greater than 4 g/cm^3 or 5 times or more, greater than water. The main sources of heavy metal contamination to surface and ground waters come from industrial activities (i.e. tannery, refinery, metal smelting), agricultural activities (the use of pesticides and fertilizers) and Mining [1-3, 7-8]. Furthermore, water systems can be contaminated by heavy metals through acid rain which breaks down the soils and rocks, releasing heavy metals into ground water resources.

The presence of heavy metals in the environment leads to a growing number of environmental problems such as the deterioration of several ecosystems due to its persistent accumulation [9-17]. Wastewater pollution by heavy metals is a common environmental hazard, since the toxic metal ions dissolved can ultimately reach the top of the food chain and thus become a risk factor for human health [9-10, 12]. These heavy metals become toxic, especially to humans when the quantity is too high and it takes really very little to be too much [7]. Toxicity also varies according to environmental conditions that control the chemical speciation of the metals

[9]. One of such heavy metals of concern is Copper. It is present in the wastewater of several industries, such as metal smelting, refineries, paper and pulp, fertilizer and wood preservatives [9-10]. Excessive intake of Copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney [9]. Beside health effects, heavy metals are non-renewable resources, and thus, their effective recovery is as important as their removal from waste streams [13-17].

Copper is an essential element for all living organisms, hence small amounts are needed in the body. Of the copper sulfate used domestically, 65% is used in agriculture for fungicides, algaecides, nutritional supplements, insecticides, and repellents; 28% is used industrially in froth flotation production of chromated copper arsenate wood preservatives, in electroplating, and in the manufacture of azo dyes; and 7% is used in water treatment to control nuisance algae [19]. Although other heavy metals (i.e. Lead, Mercury and Cadmium) are more toxic than Copper, they can easily be avoided as compared to Copper because they are not essential for plants and animal life [13-17].

Several methods have been recommended for the removal of toxic heavy metals from waste waters of the world, including chemical precipitation, coagulation, ion exchange, reverse osmosis, solvent extraction, filtration, evaporation and membrane methods [1-4, 7]. The application of such methods is somehow limited by technical and/or economic constraints such as the requirement for several pre/additional treatments [18]. In addition, some of them are less effective and require high capital cost to implement [7, 18].

In general, an adsorbent can be assumed to be "low-cost" if it requires little or no processing, is abundant in nature, or is a by-product or a waste from an industry [7]. Watermelon rinds (Figure 1) are typical agricultural products that are widely produced from in-house, restaurant and market, and are very cheap to acquire. This study, therefore, focuses on assessing the removal efficiency of Copper from wastewater by using watermelon rinds.

a b

Figure 1. *a. Watermelon; b. Watermelon rind.*

2. Materials and Methods

2.1. Preparation of Watermelon Shell/Rinds

The watermelon rinds used were obtained from fruit venders, available at Mwenge market, Dar es Salaam. These watermelon rinds were selected according to the National Watermelon Promotion Board [20], of which both white and green parts (exocarp) were used (Figure 2). All materials were washed repeatedly with distilled water to remove dust and soluble impurities and were allowed to dry at sun light for 48 hours. The shells were then kept in an air-oven at 333-343 K for 4 hours.

Figure 2. *Watermelon rinds preparation.*

The dried rinds were then converted into fine powder by grinding with a mechanical grinder. The powder was then sieved to get the adsorbent with different sizes (0.18, 0.4, 0.8, 1, 1.6 and 2 mm), after drying for several hours at room temperature. Finally, the powder prepared was preserved in airtight foil papers (Figure 3) for future use as adsorbents.

Figure 3. *Drying, grinding and sieving of adsorbents.*

2.2. Chemical Composition of Watermelon Shell/Rinds

The watermelon rinds were analyzed for chemical composition based on essential nutrients for plant growth such as Iron (Fe), Manganese (Mn), Zinc (Zn), Copper (Cu), Boron (B), Calcium (Ca), Magnesium (Mg), Phosphorus (P) and Potassium (K), Chloride (Cl) and Sulfate (SO_4). The chemical composition was determined through extraction of metal process in which the mixture of concentrated Hydrochloric acid and Nitric acid (aqua regia) solution in 3:1 ratio, respectively were mixed in a test tube with 0.5 g of watermelon rinds with particle size of 2 mm. The mixture was then placed in an oven for 1 hour, then left to cool, and then 10 ml of distilled water was added. After the mixture was soaked for 24 hours, it was filtered and the Atomic Absorption Spectrophotometer (AAS) was used for metal analysis. Extraction of Sulphate was done through mixing 100 ml of distilled water with 10 g of watermelon rind material, then the mixture was left overnight and was then analyzed in spectrophotometer by the addition of sulfa ver 4. reagent. For Chloride determination, 15 g of the materials were mixed with 150 ml distilled water then the samples were place on a 66°C hot plate and were stirred with magnetic stir over 15 hr digestion time and then 100 ml were titrated.

2.3. Point of Zero Charge (pHpzc)

The point of zero charge (PZC) also acronymed pHpzc means the pH at which the total number of positive and negative charges on its surface becomes zero [21]. In this study, PZC was determined using the solid addition method [22] and the graph of initial pH (pHo) against the difference between the initial (pHo) and final (pH_f) pH values were plotted (Figure 14).

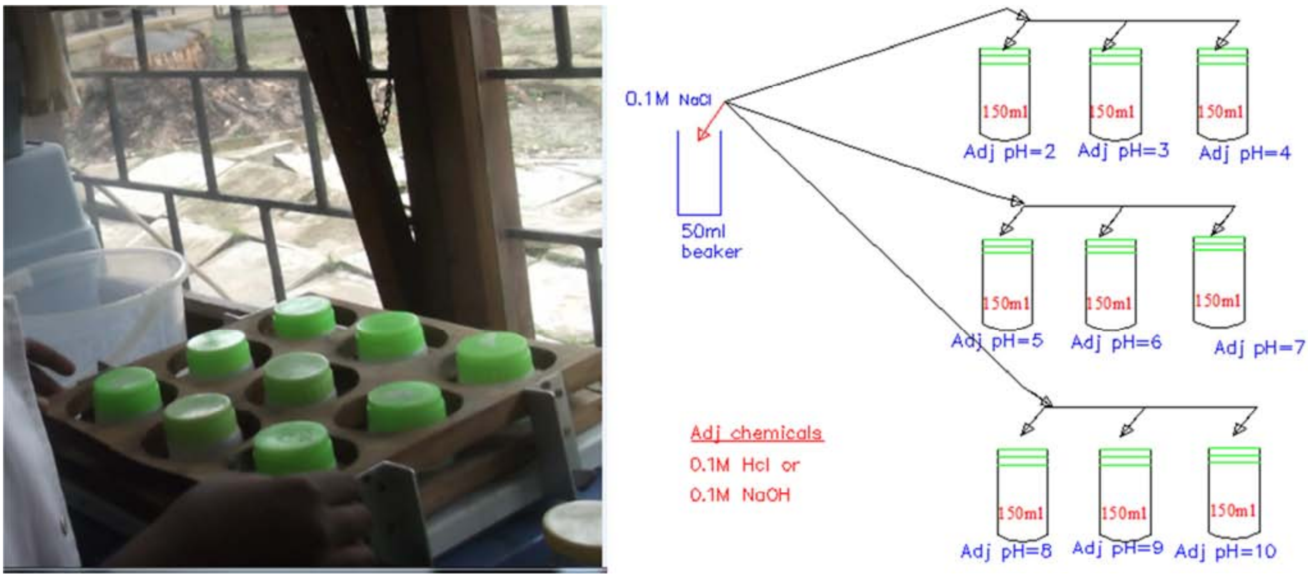

Figure 4. *Experimental setup for the determination of point of zero charge (pHpzc).*

2.4. Experimental Set up

The contaminated wastewater sample with controlled Cu (II) concentration was used. The Cu (II) concentration used was 15.72 mg/L.

2.4.1. Batch Experimental

The experimental setup involved a batch reactor experiment, using beakers, to determine the effect of pH, contact time, particle size and the quantity of adsorbents to treat a unit volume of the wastewater (Figure 5), as described by Mwegoha and Lema [18]. The experiment was done in triplicates.

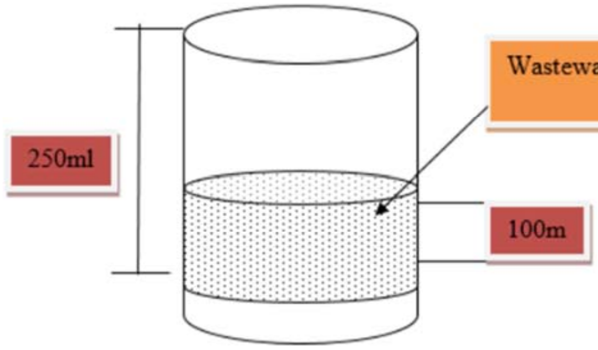

Figure 5. *Experimental setup.*

2.4.2. Determination of Adsorption Characteristics

The adsorption characteristics that were determined in the laboratory, involved; pH, contact time, particle size and dosage of the adsorbent. The experiments were performed in duplicate form for each parameter using batch reactor. Figures 4, 5, 6 and 7 describe different adsorption characteristics, in relation to Copper II removal from synthetic wastewater.

Six 50 ml solutions of initial concentration (15.72 mg/l) of Copper prepared from the salt of Copper ($CuCl_2.2H_2O$) were placed in 250 ml conical flasks. Different samples of masses; 0.05, 0.1, 0.15, 0.2, 0.25 and 3 g of 0.18, 0.4, 0.8, 1, 1.6 and 2 mm sizes respectively, were added in the solutions. NaOH base and HCl acid solutions were used to alter pH of the solution from 6.8 to 9.35. The first experiments were conducted for adjusted pH of 6.8, 7.52 and 9.35, whereby particle sizes and doses were varied. The solutions were stirred by magnetic stirrer on the hotplates at 350 rpm, and the contact time was varied from 30 to 120 min. Treated wastewaters were filtered by using the Whattman filter papers (grade No. 42) before analysis for Copper (II) ions was done in Atomic Absorption Spectrophotometer (Figure 13). All parameters were varied until the optimum pH, dose, and contact time were obtained as shown in Figures 15-17. All adsorption experiments were carried out at the room temperature (25°C).

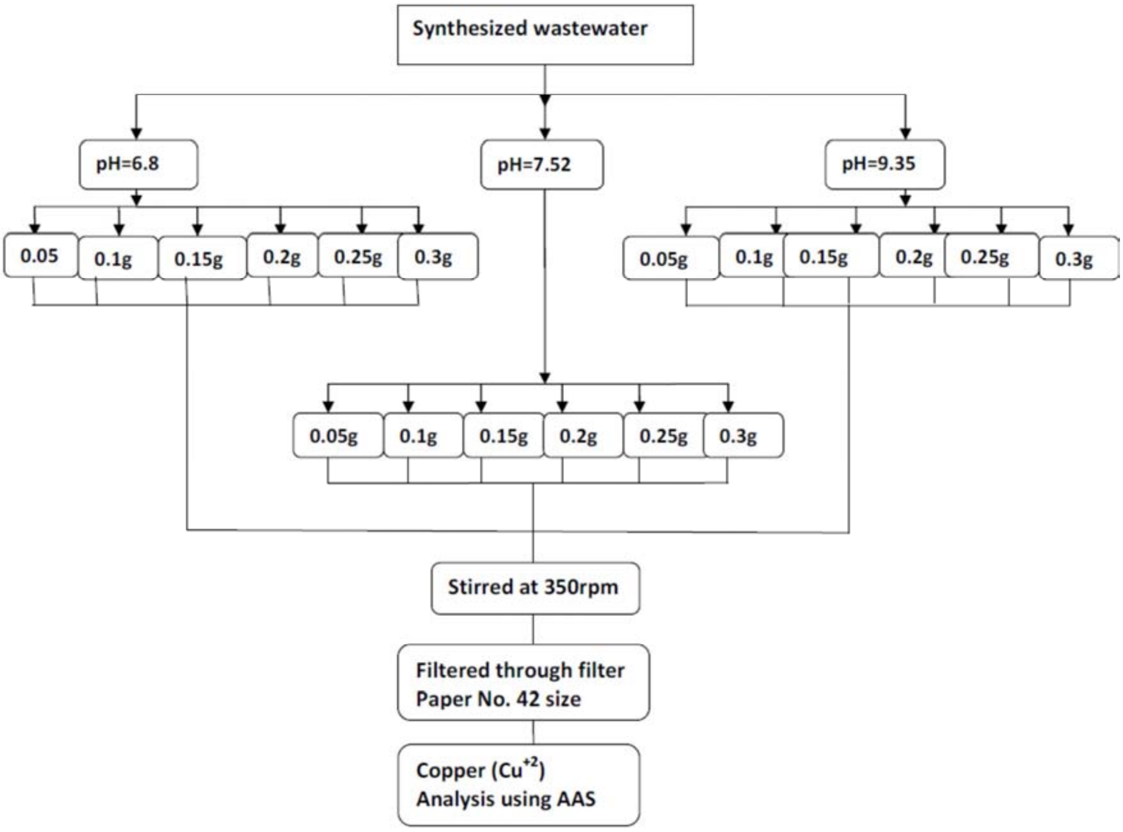

Figure 6. *Batch experiment layout showing the effect of dose and pH on the removal of Cu^{2+}.*

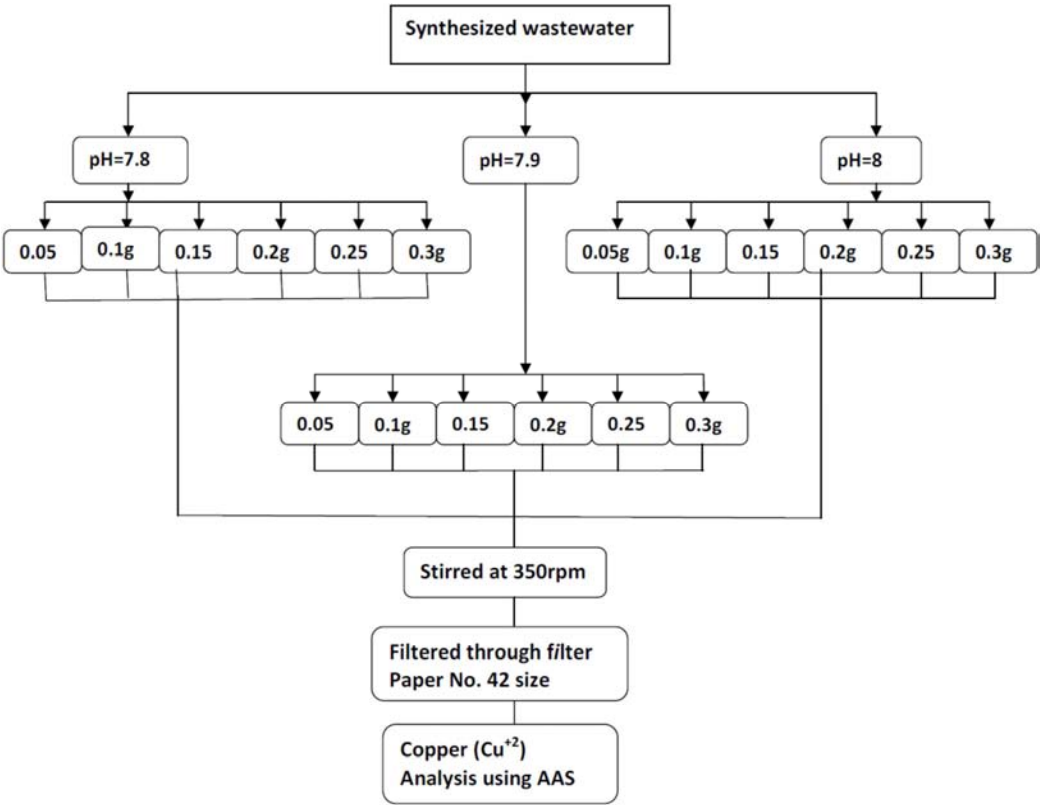

Figure 7. *Batch experiment layout showing the effect of dose and pH on the removal of* Cu^{2+}.

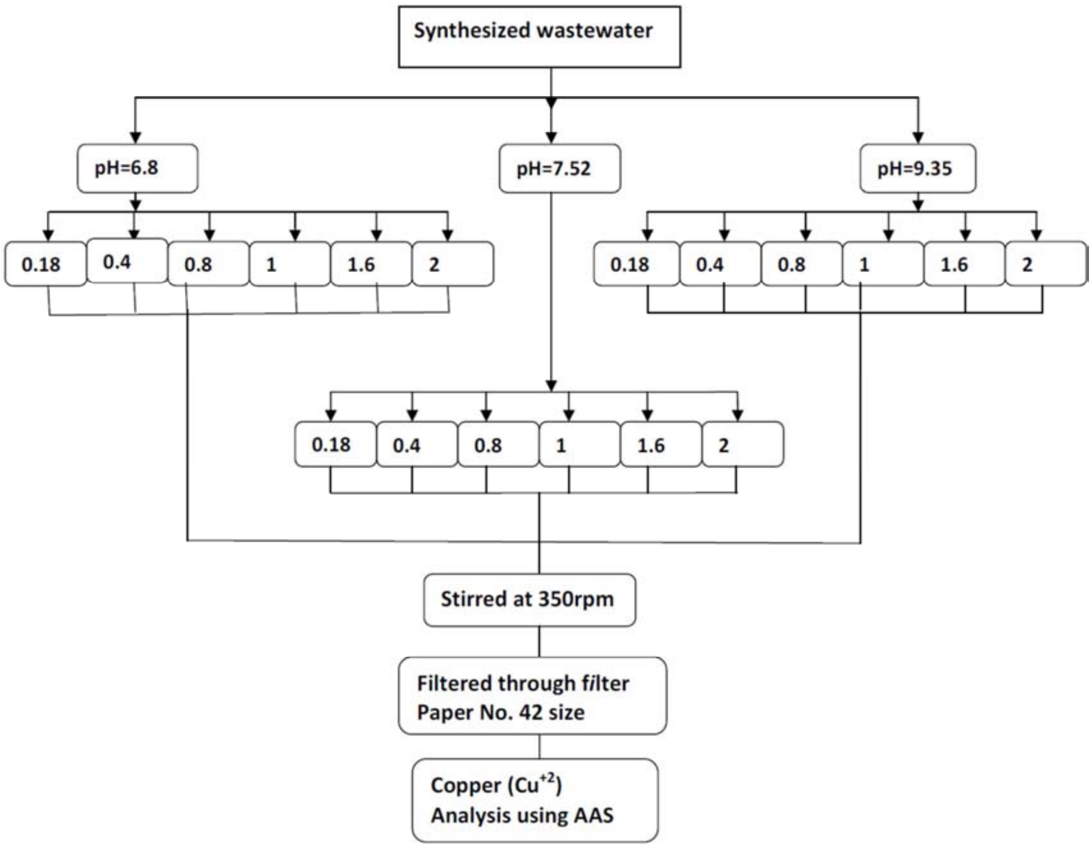

Figure 8. *Batch experiment layout showing the effect of particle size and pH on the removal of* Cu^{2+}.

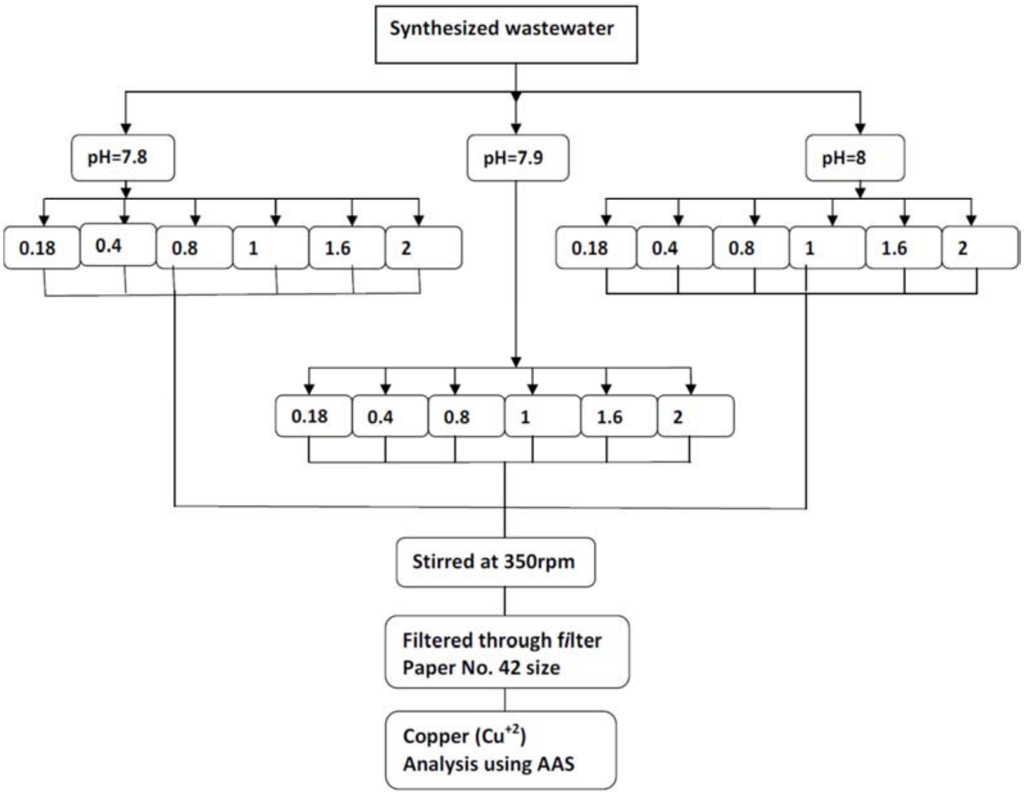

Figure 9. *Batch experiment layout showing the effect of particle size and pH on the removal of* Cu^{2+}.

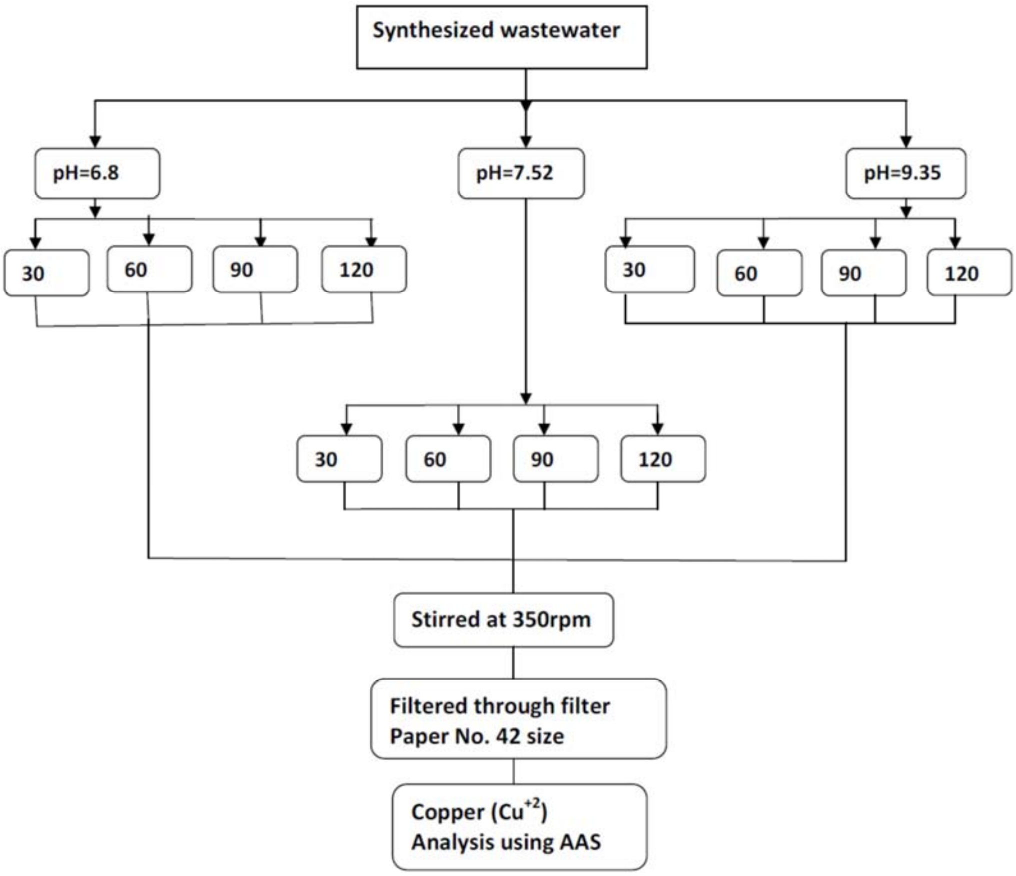

Figure 10. *Batch experiment layout showing the effect of contact time and pH on the removal of* Cu^{2+}.

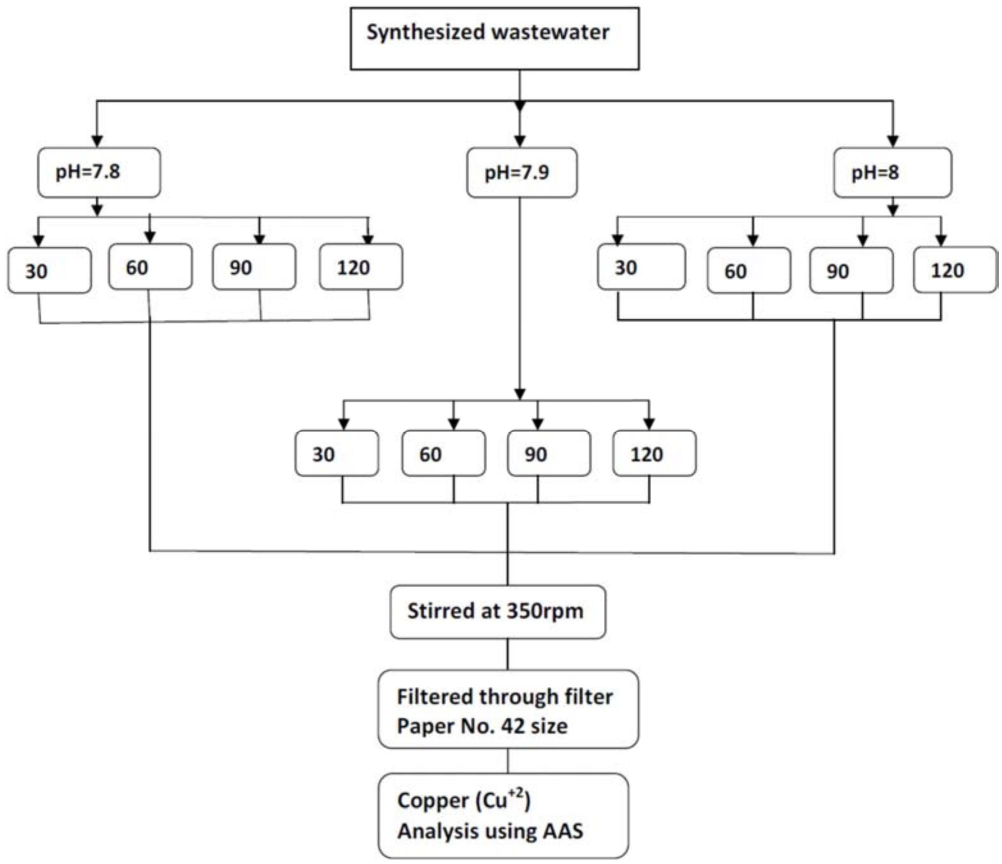

Figure 11. *Batch experiment layout showing the effect of contact time and pH on the removal of* Cu^{2+}.

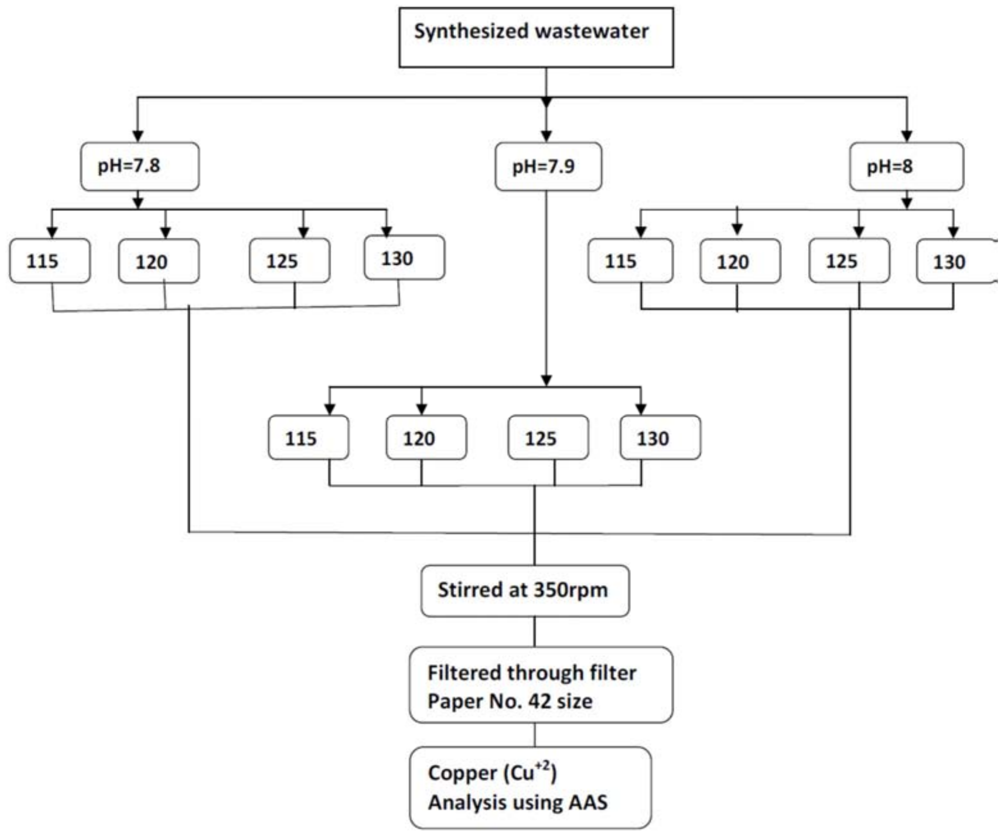

Figure 12. *Batch experiment layout showing the effect of contact time and pH on the removal of* Cu^{2+}.

Figure 13. Sample preparations for the analysis of Cu^{2+} using AAS.

2.5. Data Analysis

The analysis of data was performed using descriptive statistics including histograms, percentage and linear regression. These were managed through the use of MS (Microsoft Office) Excel, 2013. Also Freundlich and Langmuir adsorption isotherms and capacity were used to determine the favorability of the data obtained.

3. Results and Discussion

3.1. Point of Zero Charge Results

Results show that the zero point of charge of the watermelon rinds is at a pH of 5.9 (Figure 14). This result is in good agreement with the data reported in the literature regarding PZC [21-23].

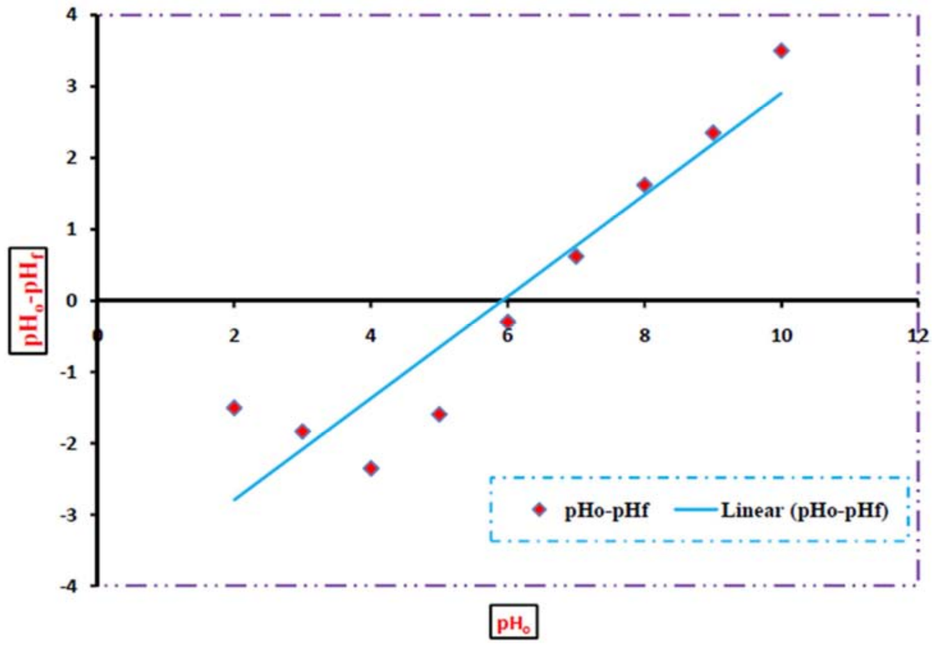

Figure 14. Shows the Point of Zero Charge for Water melon.

3.2. Characteristics of the Adsorbent

The results obtained in this study are shown in Table 1. The moisture content was 89.79 g and electrical conductivity was 17 ms/cm.

Table 1. The micro-nutrients and macro-nutrient available in watermelon rinds.

Parameters	Ca	Fe	Cu	Zn	Mg	S	K	Cl
Conc (mg/l)	1100	0.36	0.32	0.29	990	4900	5200	1410

3.3. Efficiency of Watermelon Rinds to Remove Copper (II) Ions from Synthetic Wastewater

Watermelon rinds' efficiency to remove Copper (II) ions from synthetic wastewater was studied through optimization of the following parameters; pH, particle size, contact time and dosage. The results were as follows;

3.3.1. Effect of pH

The pH is amongst one of the important parameters for adsorption process as it controls the protonation of the functional groups on the biomass as well as the metal chemistry. Therefore the influence of pH on Cu (II) ions biosorption by watermelon rinds was investigated in the pH range; 2.0–10.0. Biosorption potential of watermelon rinds for Cu (II) was seen to increase with an increase in solution pH and it was observed that at pH less than 5.9 the surface of the watermelon rinds is predominated by positive charges while at pH greater than 5.9 the surface is predominated by negative charges. Thus, below pH 5.9, the material surface has a high positive charge density meaning the uptake of positively charged Copper is low. With increasing pH (beyond PZC), the negative charge density on the surface of the adsorbent increases causing the negatively charged surface favor the adsorption of Copper cation due to electrostatic attraction.

Furthermore, it was investigated that at a pH of 7.9, biosorption potential of watermelon rinds for Cu (II) started to decrease slowly. This was attributed by the precipitation of Cu (II) as $Cu(OH)_2$. [24].

3.3.2. Effect of Contact Time

Contact time seemed to affect the extent of adsorption of the Cu (II) ions from synthetic wastewater. As it can be seen from Figure 15, the amount of the adsorbed Cu (II) onto the watermelon rinds increases with time and, at some point of time, it reaches a constant value beyond which no more Cu (II) is removed from the solution. At this point, the amount of the Cu (II) ions desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the metal being adsorbed onto the watermelon rinds [25]. The maximum removal of 98.98% at equilibrium time of 120 minutes was attained.

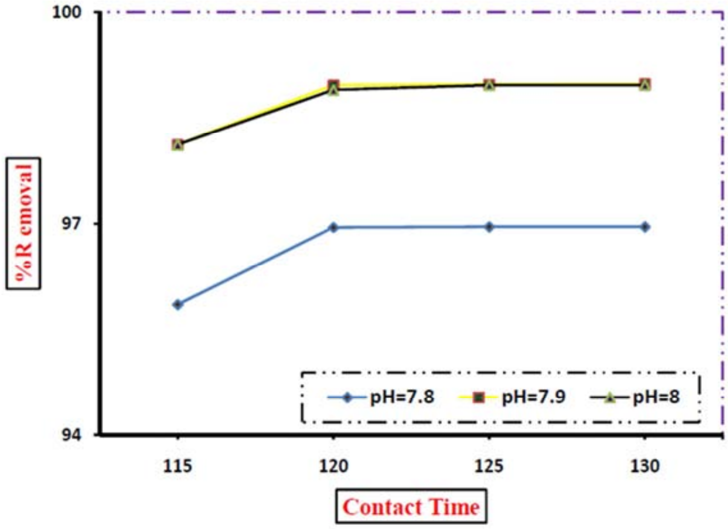

Figure 15. *Effect of contact time on removing Cu^{2+} from synthetic wastewater.*

3.3.3. Effect of Particle Size

At optimal pH and contact time, the removal of Cu (II) at different particle sizes showed that the removal rate increased with a decrease in particle size as shown in figure 16. The relatively higher adsorption with smaller adsorbate particles (0.18 mm) may be attributed to the fact that smaller particles yield large surface area, which provides more biosorption sites for the metal ions. For larger particles (0.3 mm), the diffusion resistance to mass transport is high and most of the internal surface of the particle may not be utilized for adsorption and consequently, the amount of Cu (II) adsorbed is small. Similar trend has been reported in the literature [25-27].

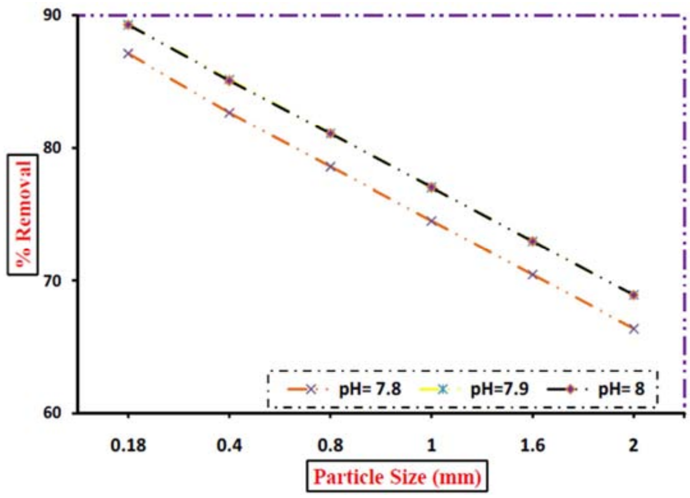

Figure 16. *Effect of particle size on removing Cu^{2+} from synthetic wastewater.*

3.3.4. Effect of Dose of Adsorbent

At optimal pH, particle size and contact time, the adsorption of Cu (II) ion by watermelon rinds was studied by changing the quantity of watermelon rinds (0.05 - 0.3 g) while keeping the initial Cu (II) concentration (15.72 mg/L). The increase in adsorbent dosage increased the percent removal of Cu (II) (Figure 17), which is due to the increase in absorbent surface area of the adsorbent. At the dosage of 0.2 g, the change in concentration is very small and this is due to high watermelon rinds concentration in the solution which can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase dose of the adsorbent [25]. The maximum removal was found to be 98.97% at the dose of 0.2g/50ml.

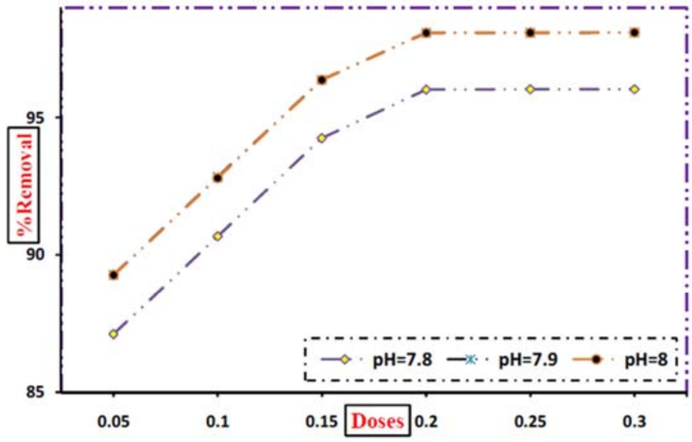

Figure 17. *Effect of dosage on removing Cu^{2+} from synthetic wastewater.*

3.4. Adsorption Isotherms

Experiments were conducted to determine the adsorption isotherm of Copper using watermelon rinds at 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g in 50 ml of synthesized wastewater with pH 6.8, 7.52, 7.8, 7.9, 8 and 9.35. Initial Copper concentration was 15.72 mg/l.

The experimental data were calculated to determine the adsorption isotherm using the Freundlich model and Langmuir model. The effects of different watermelon rinds dosages on the adsorption of Copper were found to correspond to both Freundlich and Langmuir adsorption isotherm [28].

$$\mathrm{Log}\frac{X}{M} = \frac{1}{n}\mathrm{LogC_e} + \mathrm{LogK_f}$$

And the plot of $\frac{1}{X/M}$ versus $\frac{1}{C_e}$ yields a straight line, which implies that the adsorption process conforms to Langmuir equation.

$$\frac{1}{X/M} = \frac{1}{q_{max}b}\left(\frac{1}{C_e}\right) + \frac{1}{q_{max}}$$

In this equation, X/m is the amount of Copper adsorbed per dose of watermelon rinds, Ce is the equilibrium concentration of Copper in solution, K and 1/n are empirical constants (Freundlich parameters); the values of which are equal to the intercept and slope of the plot of log X/m versus log Ce. Log X/m versus log Ce was plot as shown in the Figure 18 and 19. At optimal conditions, the correlation coefficients (R^2) were found to be 0.929 and 0.87 for Freundlich and Langmuir isotherms, respectively. These values are between 0.7 and 1.0, which shows that watermelon rinds are good for Cu (II) ions adsorption [29].

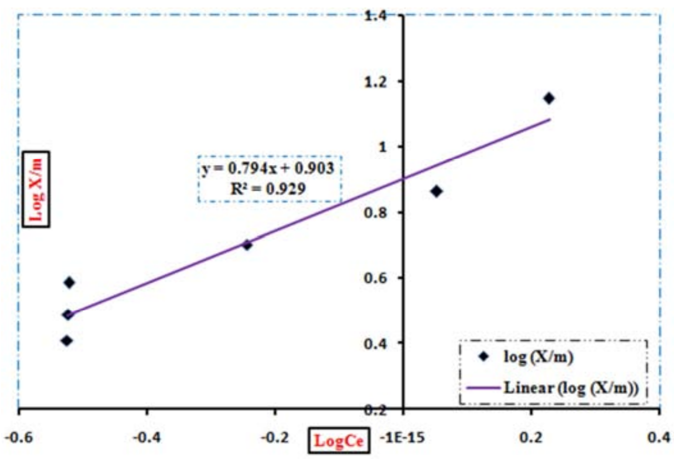

Figure 18. *Freundlich isotherm for Cu^{2+} removal by watermelon rinds.*

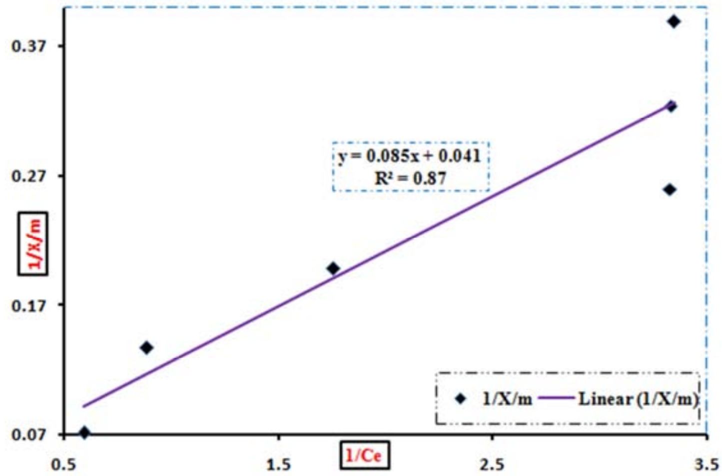

Figure 19. *Langmuir isotherm for Cu^{2+} removal by watermelon rinds.*

From Figures 18 and 19, regression values (R^2) indicate that the adsorption of Cu (II) ions by watermelon rinds fits well with the Freundlich and Langmuir isotherms, out of which Freundlich adsorption model was found to have the highest regression value and hence the best fit.

3.5. Adsorption Capacity

The adsorptive capacities of the adsorbents were estimated by extending a vertical line from the point on the horizontal scale corresponding to the initial concentration Co and extrapolating the isotherm to intersect this line. The $(x/m)_{Co}$ value at the point of intersection was read from the vertical scale. Therefore, $(x/m)_{Co}$ value represents the amount of contaminant adsorbed per unit weight of the adsorbent when the adsorbent was at equilibrium with the initial concentration of adsorbate (contaminant); Co equals to 15.72 mg/L [1]. Therefore, the adsorption capacity from this study (Figure 20) is 115.3mg/g.

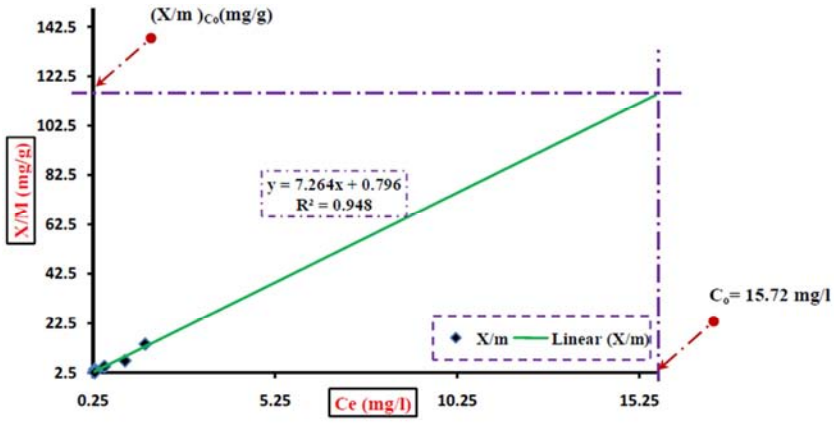

Figure 20. *Adsorption capacity for Cu^{2+} removal at pH 7.9 (X/m).*

4. Conclusion

From this study, it is demonstrated that watermelon rinds are potentially suitable adsorbents for Cu (II) ions removal from wastewater. The zero point of charge of the watermelon rinds was obtained at a pH of 5.9, optimum pH was at 7.9, optimum dosage of watermelon rinds was 0.2 g/50 ml (with an initial Copper concentration of 15.72 mg/l) and the optimum contact time was approximately 120 minutes. The final concentration of Copper at optimum conditions was 0.115 mg/l, which is lower than the recommended limits for municipal and industrial wastewaters of 2.0 mg/l [30]. Adsorption equilibrium was better described by the Freundlich model (0.929) than the Langmuir isotherm model (0.87). On an overall perspective, the present findings suggest that watermelon rinds are environmentally friendly, efficient and low-cost biosorbents which are potentially useful for the removal of Cu (II) from aqueous media.

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