## **Adsorption Isotherms and Kinetics Studies on Adsorption of Copper onto Modified and Unmodified biomass tea waste from Wastewater in Kisii County, Kenya**

 **ABSTRACT**

Among the most hazardous environmental issues nowadays is heavy metal pollution. One efficient technique for eliminating wastewater that contains heavy metals is adsorption. In order to assess an adsorbent's effectiveness and construct an adsorption system, the maximal adsorption capacity, the adsorption process and the movement of mass phases can all be determined in kinetics models and adsorption isotherms. This study examined tea waste treated with sulfuric acid as an inexpensive alternative adsorbent for the removal of Cu (II) ions from aqueous solution. 1M H2SO4 was added to the tea waste, and it was heated to 150°C for 24 hours. Tea waste and tea factory wastewater was taken from Nyamache tea Factory.The adsorption kinetics and isotherms of heavy metals by both modified and unmodified biomass tea waste were compiled and thoroughly examined in this paper. biomass quantity (0.1 to 1.0 g), pH levels (2.0 to 10.0), all had an impact on the biosorption procedure. The findings from the study show the optimum values for adsorbent dosage as 0.7 grams and pH as 6. The adsorption capacities of modified and unmodified tea waste were 14.144 and 12.706 respectively, the adsorption capacity for modified tea waste were comparatively greater than those of unmodified tea waste. For both modified and unmodified tea waste, the adsorption data fit the Langmuir isotherm model better than the Freundrich model, with correlation coefficients of 0.9477 and 0.9402, even though the adsorption kinetics matched pseudo-second-order kinetics (R=0.9999). The findings show that copper (ll) ions can be removed from household wastewater by using modified tea waste.

*Keywords. Heavy metals, Adsorption kinetics, Adsorption isotherm, Wastewater.*

**1. INTRODUCTION**

Around 1.2 billion people globally are thought to consume tainted water. which contributes to the 5–50 million deaths from water-borne illnesses (Nthiga et al., 2016). Around 17 million individuals (43%) in Kenya lack access to potable water (Wanja et al., 2016). Recurrent drought, inadequate water supply management, and contaminated accessible water as a result of rapid population increase have all contributed to Kenya's severe water deficit. Compared to metropolitan areas, where 88% of people have access to safe water, only 42% of people in rural areas have this luxury (Mulei, 2012).

According to Alqadami et al. (2017), the majority of heavy metals are very poisonous, detrimental to all varieties of life, and not recoverable by biological mechanisms. They also tend to build up in creatures that live through the food chain (Xiao et al., 2017). These metals have the potential to cause cancer as well as damage to the brain, bones, and neurological system (Rao and Khatoon, 2017). In an adequate quantity, copper is a necessary trace element for a healthy body (Joseph et al., 2013). Numerous symptoms, including development retardation, skin conditions, gastrointestinal issues, gradual liver malfunction, pancreatic damage, and the onset of Wilson disease, are caused by its high absorption, which may be detrimental to human health (Nthiga et al., 2021). Anorexia and weakness can also result from high copper concentration (Kumar et al., 2014), According to Koel et al. (2012), itching, derrnatization, hand keratinization, and lung cancer can all result from extended exposure to copper spray. The World Health Organization (WHO) set a maximum permissible copper concentration in drinking water of 2.0 mg/L in 2006.

 One heavy metal that is used extensively in the plumbing, roofing, air conditioning tube, and electrical wiring industries is copper. Copper is ideal for various applications and is indispensable in industry due to its unique qualities, which include high electrical and thermal conductivity, ease of fabrication and installation, superior corrosion resistance, appealing appearance, and high recyclability. Aqueous wastes from a variety of industries, including the fertilizer industry, pulp and wood pulp manufacturing, metal cleaning and plating baths, and paper board mills, contain Cu (II) pollution. As a result, these industries' effluent must be treated before being released into the water stream (Nyaboke et al., 2017).

Numerous studies on the remediation process have been conducted and continue to be undertaken in fields like filtration, membrane processes, sedimentation, precipitation, coagulation, flocculation, flotation, electrochemical approaches, biological methods, reactions of chemicals, exchange of ions, and absorption (Archibong et al., 2024). However, adsorption is the technique that many researchers have described as being very selective, effective, simple to use, and economical (Ndung,et al., 2020). The surface shape, polarity, pore size distribution, adsorbent surface area, and functional groups attached to the surface are all factors that influence adsorption, an alternate method for removing heavy metals at low concentrations. The capacity of numerous low-cost adsorbents for recovering water that contains heavy metals has led to their selection. Adsorption has therefore been employed as a less costly method of water treatment (Wanja et al., 2016). However, in important counties like Kisii, which is undergoing tremendous industrial growth, particularly in the agricultural sector, no concrete study has been done on the use of biomass tea waste treated with sulfuric acid as an inexpensive adsorbent for wastewater treatment for removal of copper (ll) ions.

Thus, it was necessary to find reliable and environmentally safe alternative for adsorbents, which is why using tea waste as a possible strategy in our study was necessary.

The link between the aqueous concentrations and the adsorbed at equilibrium is commonly studied using equilibrium removal of specific metal ions in relation to adsorption isotherm models (Ashraf *et al.,* 2011). Isotherms for equilibrium adsorption which are defined by a specific constant whose values express the appearance characteristics and affinity of the adsorbent for various pollutants, can be used to characterize the ability of an adsorbent to absorb (Madivoli *et al.,* 2016). We employed adsorption isotherm models: the Langmuir and Freundlich isotherm model, they were chosen for this investigation in order to fit the experimental data. Experimental results for Cu (II) ions in a single metal system were analysed using the Frendlich and Langmuir equation versus initial concentration for both unmodified and modified tea waste. Analyzing the effects of adsorbent dosage and pH on the removal of Cu (ll) ions, and fitting the findings to adsorption isotherms and studying the kinetic studies were the goals of the current study.

**2. Materials and methods**

**2.1 Chemicals and Reagents**

Every chemical utilized was of analytical purity. (Purity > 98.9%) purchased commercially from PYREX East Africa Limited, which has a branch in Nairobi, Kenya.

**2.2 Preparation of adsorbent**

After thoroughly cleaning with deionized water, the biomass tea waste was allowed to dry and heated to 105°C in an oven to get rid of any remaining moisture. It was then sieved, ground into a fine powder, and divided into two sections. In one portion, 1M sulfuric acid was added in a 1:2 weight-to-volume ratio, and the mixture was heated for 24 hours to 150° C. After cooling, distilled water was used to rinse each product to get rid of extra acid and then left overnight in 1% NaHCO3 to remove any remaining residue (Nthiga et al. 2021). After being dried at 105° C to a consistent weight, the resulting powders were labelled as MTW (modified tea waste) and UTW (unmodified tea waste) and kept in desiccators ready for use.

**2.3 Metal solution**

In volumetric flasks, certain quantities of Cu salts were dissolved in deionized water to create the solutions of copper (ll) ions. The stock solutions were diluted in order to create initial concentrations of the metal ions. Using 0.5 M HCl and 0. M NaOH solutions, the pH was brought to the appropriate level.

**2.4 Adsorption experiments**

 Using both modified and unmodified tea waste, batch adsorption techniques were performed by adjusting the adsorbent dose along with the solution's pH. To achieve the equilibrium time in adsorption studies, precise amounts of the adsorbent were added to 50 ml of waste water in conical flasks set on an orbital shaker. To investigate their impacts on the effectiveness of metal ion removal, the solution's pH (2–10) and the adsorbent dosage (0.1–1.0) g were varied, following filtration with Whatman 42 filter paper, the amounts of metal ions were analysed. The following formulas were used to determine the percentage removal and the metal intake, respectively:

 $ Q\_{e}=\frac{\left(c\_{i}-c\_{o}\right)V}{M}$………………………………………………………….2.1

 $R\% =\frac{Co-Ce}{Co}×100$……………………………………………………2.2

Qe (mg/g) is the adsorption capacity; Ce (mg/l) is the equilibrium concentration; m (g) is the mass of the adsorbent; and Co (mg/l) is the initial concentration. Adsorption isotherms Using 0.5 g of the raw adsorbent put into 50 ml of the metal ion concentrations and shaken for equilibrium time at 130 rpm, adsorption isotherms were examined for establishing metal ion concentrations ranging from 10 to 50 mg/l. The Freundlich and Langmuir isotherm models were used.

The adsorption equilibrium was analyzed according to the Langmuir and Freundlich adsorption isotherms using Eq. 3 and Eq.4, respectively.

$ \frac{c\_{e}}{q\_{e}}=\frac{1}{bq\_{max}}+\frac{c\_{e}}{q\_{max}}$…………………………………………………………………………..2.3

$ q\_{e}=k\_{f}c\_{e\frac{1}{n}}$………………………………………………………………………………….2.4

where qe is the metal ion absorbed during equilibrium (mg/g) per gram of the adsorbent. The maximal capacity for metal biosorption is denoted by qmax. For the binding site, b is the affinity constant. Ce signifies adsorbate equilibrium concentration.

3.0 RESULTS AND DISCUSSION

To demonstrate the active behaviour of any adsorbate from solution to the solid adsorbent phase, an in-depth analysis of the equilibrium state between the two phases is necessary. The adsorption isotherm, which is typically the ratio of the amount adsorbed to that which remains in the solution at a particular temperature at equilibrium, describes the equilibrium relationship between the adsorbent and the adsorbate. Using varying concentrations of the metal ions on a fixed amount of adsorbent, the absorption capacity of Cu (ll) ions in tea waste was assessed. The results and derived constants are shown in Figs. 1 and 2 below.

3.1 Effects of contact pH on Cu (II) Ions

Fig1. demonstrate that both acid-treated and raw tea waste exhibit Cu (ll) ion sorption as a function of pH. Cu (ll) ions uptake was low at low pH values and increased as pH rises, reaching a maximum sorption at 6.0 for acid-treated tea waste and 5.9 for raw tea waste. The amount of Cu (ll) ions adsorbed decreases with additional pH increases after the ideal pH is established. This can be due to the fact that at low pH hydrogen ions and copper (ll) ions compete for the available exchange sites, preventing the latter from getting close to the binding sites. (Nyaboke et al.,2025). Significant Cu (ll) ion adsorption occurred at pH 5.9 and pH 6.0.The binding sites might not have been activated in basic conditions above pH 6. (Kamau et al., 2021). The availability of Cu2+, Cu (OH)+ and Cu (OH)2+ for adsorption at this pH range explains this (Nthiga et al., 2021). In basic conditions, the binding sites might not be activated bove pH 6 (Hossain et al, 2012). Cu (ll) ions began to precipitate as Cu (OH) which cause the amouut of Cu (ll) adsorbed to decrease.

. **Fig 1: Effect of pH on removal of copper (ll) ions**

1 0

8

6

4

2

50

40

unmodified tea waste

90

80

70

60

100

Modified tea waste

pH

**3.2 Effect of dosage of adsorbent on Cu (ll) ion sorption**

The results show that the absorption of copper (ll) ions increased with increasing adsorbent dosages. The maximum intakes of raw and acid tea waste were 0.4g and 0.6g, respectively, and the percentage removal of copper (ll) ions did not increase noticeably above this mass. This behaviour can be explained by the increased surface area of adsorbents, followed by the increased availability of active sites in relation to concentration (Nyaboke et al., 2025).

1

0.9

0.8

0.7

 Mass(g)

0.4

0.3

0.2

0.1

50

40

modified tea waste

60

unmodified tea waste

100

90

80

70

0.5

0.6

**Fig 2:** **Effects of adsorbent dosage on Cu (II) ions**

After acid treatment, the maximum percentage of Cu (II) ions that were removed for untreated tea waste increased from 85% to 94%. Similar findings have been reported in other research, such as the elimination of Cu (ll) ions from orange peel and activated carbon (0.8g) by Benard and Jimol (2013), 99% in orange peel treated with acid, and 75% in raw orange peel (Khalfoui and Meniai, 2012

Table 1: Langmuir and Freundlich constants for Cu (ll) ions adsorption using modified tea waste.

|  |  |
| --- | --- |
| **Langmuir** | **Freundlich** |
| **Element** | **Qmax(mg/)** | ***b*(L/mg)** | **R2** | **KF** | **1/n** | **R2** |
| UTW | 12.706 | 0.0433 | 0.9016 | 1.342 | 0.2467 | 0.8807 |
| MTW | 14.144 | 0.0476 | 0.9477 | 1.337 | 0.4149 | 0.9402 |

**3.3 Adsorption isotherm for Cu (ll) ions using modified and unmodified tea waste**

The data fit the Langmuir model well, as indicated by the R2 = 0.9447 obtained from the sorption of Cu (II) ions with acid-treated tea waste. The Freundlich model cannot be applied to the data, as seen by the R2 = 0.9402. The chemisorption mechanism is indicated by this model, which also suggests monolayer adsorption. (Mwangi *et al*., 2012). found that lower values of b « 1) were observed from all adsorption operations, indicating the strong affinity of the adsorbent for copper. The raw tea waste had a lower adsorption capacity (qmax) of 12.7 compared to the acid-treated tea waste's qmax of 14.14. It is evident from this that the sorption capabilities of these adsorbents were enhanced by acid treatment. These findings are comparable to researchers' findings on the peels of watermelons (Koel et al., 2012), bananas (Hossain et al., 2012), and oranges (Liang et al., 2012).

For the adsorption of copper (II) ions in this adsorbent, the Langmuir model is applicable, as evidenced by the R2= 0.9016 and R2=0.8807 for Freundlich model values found in unmodified tea waste. In the adsorption process, l/n is determined by the adsorption strength, whereas the constant kf an approximation of adsorption capacity (nyaboke et al., 2025).
The fact that adsorbents in Table.1 have l/n values smaller than one, this suggests that both acid-treated and untreated tea waste can effectively remove Cu (ll) ions through adsorption. the Freundlich isotherm and Langmuir model for the adsorption of Cu (ll) ions using both modified and unmodified tea waste are displayed in Fig 3, 4, 5 and 6

**Fig 3: Adsorption isotherm for Cu (ll) ions using modified tea waste. (Langmuir isotherm)**

 **Fig 4: Adsorption isotherm for Cu (ll) ions using modified tea waste Freundlich isotherm**

**Fig 5: Adsorption isotherm for Cu (ll) ions using unmodified tea waste (Langmuir isotherm)**

**Fig 6: Adsorption isotherm for Cu (ll) ions using unmodified tea waste Freundlich isotherm.**

**3.4 Kinetic studies**

The adsorption mechanism of Cu(ll) ions was described using a variety of kinetic model

**3.4.1 Pseudo first order kinetics**

The linearized form of pseudo first order is shown in equation 3.1

ln(qe-qt) = ln(qe k1t)…………………………………………………………………………3.1

where k1 is the first order rate constant (min), qe is the adsorption capacity of the adsorbate at equilibrium (mg/g), and qt is the adsorption capacity at time t. By graphing log (qe -qt) versus t, as seen in Figures 11and 12, the values of k1 and qe are derived from the slope and intercept, respectively.

### **3.4.2 Pseudo second order kinetics**

Equation 3.2 displays the pseudo second order rate equation in its linear version.

= …………………………………………………………………………. 3.2

In this instance k2 stands for the pseudo second order rate constant, qe for the adsorption capacity at equilibrium, and qt for the adsorption capacity at time t. Plotting t/qt produced the pseudo second order rate constant, as seen in Fig 8 and 10. (Kamau et al.,2021).

 **Adsorption kinetics for Cu (II) ions**

The adsorption mechanism, which is essential for increasing effectiveness. Choosing the best operating parameters for a full-scale batch operation requires knowledge of the kinetics of solute uptake. When developing batch adsorption systems, the adsorption rate provides crucial information.

**Table 2: A comparative analysis of pseudo first and pseudo second order**

 for Cu(ll) ions for both modified and unmodified tea waste

|  |  |
| --- | --- |
| **Pseudo-first-order** | **Pseudo-second -order** |
| **[Cu]****mg/L** | **Qe****(mg/g)** | **Constant****(min-1)** | **R2** | **Qe****(mg/g)** | **Constant****(min-1)** | **R2** |
| 50 | -0.0209 | -1.0935 | 0.6101 | 0.5242 | 0.4959 | 0.9999 |
| 50 | -0.0261 | -2.178 | 0.7574 | 0.5391 | -3.0852 | 0.9999 |

For both unmodified and modified tea waste, the pseudo first order model produced low regression coefficient values: 0.6101 and 0.7574 respectively. Consequently, the adsorption of Cu (ll) onto the tea waste could not be adequately characterized by the model of pseudo first order. The pseudo second order model for modified and unmodified tea waste showed that the correlation coefficient for Cu (II) ions was 0.9999 and 0.9983, respectively. This demonstrates how well the pseudo second model explained how the metals were adsorbed by the tea waste. The data's statistical analysis showed that the Cu (II) ions adsorbed at time intervals differed significantly (P≤0.05). The computed value of F was higher than the F critical, according to the results of the ANOVA test for both metal ions (Appendices 1-2). This demonstrated that the means at various time intervals differed significantly.

Fig 7: Adsorption of Cu (ll) ions for modified tea waste using pseudo first order.

Fig 8: Adsorption of Cu (II) ions for modified tea waste using Pseudo-second-order.

Fig 9: Adsorption of Cu (II) ions for modified tea waste using Pseudo-first-order.

**Fig 10: Adsorption of Cu (ll) ions for unmodified tea waste using a pseudo-second-order.**

 **CONCLUSION**

1. The Langmuir model characterized adsorption equilibrium more accurately than the Freundrich Isotherm models.
2. A chemisorption process was inferred by coefficients (R2), which verified that The adsorption kinetics of both modified and unmodified tea waste fit pseudo-second-order with R2 (0.9999)
3. The adsorbent's efficiency in eliminating Cu (ll) ions was significantly influenced by the pH of the solution and the amount of adsorbent

 **DISCLAIMER**

The authors hereby state that no generative AI tools, including text-to-image generators and large language models (ChatGPT, COPILOT, etc.), were utilized in the authoring or editing of this work.

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 **APPENDICES**

## **Appendix 1: Variation (ANOVA) for the effect of pH for Cu (ll) ions removal**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source of variation  | SS | DF | MS  | F | P-Value | F- Critical |
| **Between Groups** | 184.234 | 1 | 184.234 | 86.33 | 1.9E-10 |  |
| **Within Groups** | 83.346 | 36 | 2.134 |  |  | 4.11 |
| Total | 267.580 | 37 |  |  |  |  |

## **Appendix 2: Variation (ANOVA) for the effect of sorbent mass for Cu (ll) ions removal**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source of variation  | SS | DF | MS  | F | P-Value | F- Critical |
| **Between Groups** | **2.3457** | **1** | **2.3457** | **45.35** | **2.56-08** |  |
| **Within Groups** | **1.8456** | **35** | **0.0517** |  |  | **4.12** |
| Total | 4.1913 | 36 |  |  |  |  |