Elimination of Cadmium from wastewater using modified and unmodified tea waste in Kisii County, Kenya

ABSTRACT

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|  Heavy metals are a major source of water pollution in developing countries. One inexpensive technique for removing heavy metal ions from aqueous solutions is adsorption with a cheap adsorbent. This study focused into sulfuric acid-modified tea waste as a low-cost alternative adsorbent for removing Cd (II) ions from aqueous solution. The tea waste was modified using 1M H2SO4 at a temperature of 150°C for 24 hours. Tea factory wastewater was taken from Nyamache in Kisii County.The findings from the study show the optimum values for initial ions concentration as 70 mg/l, adsorbent dosage as 0.7 grams pH as 6 and contact time as 95 minutes. It was discovered that adsorption isotherms suited well in Langmuir model (R2=0.9961) than Freundlich model (R2=0.9954). the adsorption capacities for modified tea waste were relatively higher compared to unmodified tea waste, 6.7159 and 5.359 respectively. FT-IR analysis of the biomass tea waste showed the presence of O-H at a maximum of 3395 cm-1, COO- at a maximum of 2448 cm-1, C=O at a maximum of 1594 cm-1, and P-OOH at a maximum of 1216 cm-1. The existence of these functional groups on modified tea waste improved the removal of Cadmium (II) ions. SEM analysis showed the development of distinct pores on modified tea waste following treatment with sulfuric acid which also enhanced the efficacy of modified tea waste. The result reveal that modified tea waste can be applied to eliminate Cadmium from waste water in our homes.  |

*Keywords: adsorption; concentration; functional groups; heavy metal*.

1. INTRODUCTION

Water is a necessary component of life and has a major effect on environmental and public wellbeing in addition to being the basis for the majority of our economic endeavors. According to the United States Public Health Service (USPHS), contaminated water is defined as having any kind of external material, (natural and artificial) radioactive, or biological) that has the tendency to lower the water's quality to the point where it becomes dangerous. About 25% of people on the entire globe do not have access to clean water. Furthermore, one-fourth of the world's population, or 1.92 billion people, live in countries with inadequate infrastructure for bringing water from aquifers to homesteads (Ochongo *et al.,* 2019).

Since they have elevated concentration of poisoning and threat to both humans and animals, heavy metals are the primary environmental contaminants (Nyaboke et al., 2017). Numerous pathways allow contaminants to enter the systems, including mining operations, residential wastewater, and runoff from agriculture. This increases the number of species that are metallic discharged into the ecosystem (Churong et al., 2013).

 Cadmium is regarded as a very hazardous metal with no recognized biological purpose, The most common method of Cadmium exposure occurs in human is through consuming a food or drinking water that contains cadmium. Another method that individuals can be exposed to cadmium is through cigarette smoking, burning garbage, and burning fossil fuels (new bigging *et al*., 2015). Excessive levels of cadmium within the human body might result in infertility, immune system damage, mental illnesses that cause abnormalities in the mind, and stomach pain (Mohod and Dhote, 2013) The buildup of cadmium throughout the human body, particularly in the kidneys, can result in kidney dysfunction, high blood pressure, liver disease, severe lung damage, and damage to the brain and nerves are just a few of the detrimental health impacts that can result from excessive cadmium exposure, Alopecia anemia, emphysema, learning disabilities, headaches, development retardation, and arthritis are some of the symptoms (Sathish *et al*., 2014).

 Cadmium has lately surpassed lead and mercury as the most hazardous heavy metal that causes harm to the health of people and the surroundings because of its acute toxicity (kumar *et al.,* 2014). Dust from mulberry wood treated with HCI acid has been used to study the biosorption of cadmium on aqueous solution (Shah *et al.,* 2011). Exposure to heavy metals over recommended levels in humans can cause kidney damage, reported in Kenya (Nyaboke *et al.,* 2017). Depending on the species, dosage, and duration of exposure, elevated levels and accumulation of heavy metals can have very detrimental effects; they have been shown to be deleterious and cancerous. (Aendo *et al.,* 2022). Exposure to cadmium from contaminated wastewater that is released into water bodies can damage aquatic ecosystems and could enter the food chain, endangering human health, (Khan et al., 2017)

Heavy metal ions may be removed from solutions in water using several methods related to chemical, biological, and physical processes (Kumar *et al.,* 2014). Several methods for treatment of water for instance ion exchange, adsorption, filtration, solvent extraction, coagulation, and chemical precipitation have been used (Archibong et al., 2024). The high cost of the conventional physicochemical methods has prompted increasing interest in conducting research on employing low-cost alternative mechanism and one of the methods is adsorption which has been found to be economically viable, convenient, easy operation, simple in design, ecofriendly in nature and has excellent performance (Ndung’u et al.,2020). Many inexpensive adsorbents have been selected based on their ability to obtain heavy metals from water. For this reason, adsorption has been used as a less expensive technique of treating water (Nthiga et al., 2021). However, no concrete research on the use of biomass tea waste treated with sulfuric acid as a less expensive (absorbent in heavy metal removal from wastewater has been conducted in major Counties such as Kisii which is experiencing rapid growth of industries especially in the agricultural sector. Therefore, there was need to look for alternatives adsorbent which are reliable and ecofriendly and hence the need to use tea waste in our study as a possible strategy.

The adsorption isotherms provide the finest description of the removal of heavy metal ions from aqueous solutions. Relations between the quantity of metal ions that remain in the aqueous solution after equilibrium is reached and the metal ions that have stuck to the adsorbent surface are provided by adsorption isotherms. As a function of the initial metal ion concentration, the adsorption isotherm will thus tell us about the relationship between the metal ions that have adhered to the surface of the modified tea waste and unmodified tea waste and the metal ions that are still present in the aqueous solution after equilibrium is reached (Wong et al., 2014).

 The objective of the present investigation was to characterize the low cost modified and unmodified biomass tea waste, examining the impact of adsorbent dose, initial metal ion concentration, contact time, and pH on the removal of Cd (ll) ions, and fitting the results to adsorption isotherms.

**2.0 MATERIALS AND METHODS**

 **2.1 Reagents and Chemicals**

All of the reagents and chemicals utilized had analytical quality. (Purity > 98.9%) . Every solution was made using double-distilled water. 0.1M Sodium Acetate, Soluble metal salt of Cd2+ and as well as KNO3 NaOH, HCl, H2SO4, sodium acetate, sodium bicarbonate and potassium bromide were among the chemicals used and were commercially purchased from PYREX East Africa limited with its branch located in Nairobi Kenya.

**2.2 Standard solution and stock solution preparation**

Cd2+ stock solution with concentration of 1000 ppm was made from the corresponding salt. Distilled water in a 1000 ml volumetric flask was utilized to dissolve 1.8759g of Cd (NO3)2.5H2O, to create the stock solution. Using commercial buffer tablets (pH 4 and 7) and a pH meter (model Hanna GLP 110), the model solution was made with the necessary metal ions under investigation and adjusted to pH 5. Acetic acid and sodium acetate were used to make the acetate buffer Distilled water was added to the solutions until they reached the 1000 cm-3 level. To create the working solution distilled water was used to dilute the stock solutions to the appropriate concentration.

**2.3 Preparation of the adsorbent**

Biomass tea waste was locally collected from Nyamache tea factory in Kisii County. The biomass tea waste was taken to the Jomo Kenyatta University of Agricultural and Technology laboratory.  It was extensively cleaned using deionized water and then allowed to dry to remove moisture in an oven preheated to 105°C, Sieved and ground into a fine powder and finally separated into two portions. One portion was handled with 1M H2SO4 in a ratio of 1:2 weight-to-volume. The mixture was heated to 150°C for 24 hours to get rid of the residue. After cooling distilled water was used to rinse each product to get rid of extra acid, and then left in NaHCO3 (1%) for the entire night (Nthiga et al., 2016). The modified tea waste was then dried to a consistent weight at 105°C. The resultant powders were finally stored in desiccators ready for use. They were marked as MTW (modified tea waste) and UTW (unmodified tea waste).

## **2.4 Surface Characterization**

FTIR spectra using the SHIMADZU FTIR 8400S (Kyoto, Japan) was used to characterize the functional groups found in tea waste. 1mg of dried tea waste both treated and untreated, was combined with 50 mg of KBr (1:50) to create the FTIR analysis samples. The mixture was vacuum-pressed after being finely powdered into a pellet. FTIR spectrophotometer was then used to analyze the pellet. The measurement range for the adsorbents' spectra was 600–4000 cm-1. Prior to and following acid treatment, spectra were plotted on the absorbance axis using the same scale.

**2.5 Sem Analysis**

The texture and surface morphology of the both MTW and UTW was determined using the Scanning Electron Microscope.

**2.6 Instrumentation**

 The instruments that were used include; An air-acetylene flame Shimadzu AAS Model AA 7000, a spectrophotometer for flame atomic absorption, pH meter (pH 211, Hanna instruments), Fourier transform infrared spectrophotometer (Shimadzu, Japan, Model FTS-8000), Mechanical shaker and Scanning Electron Microscope.

**2.7 Adsorption studies**

To assess the effectiveness of using modified tea waste and unmodified tea waste to remove cadmium from aqueous solutions, batch tests were conducted. The primary factors influencing bio-sorption, including adsorbent dose, initial metal concentration, pH and contact time were assessed. The stock solution was salt of cadmium metal standard at 1000 mg/l. To create the working solution, the stock solutions were diluted with distilled water to the appropriate concentration.

The sorption results were used to calculate the metal uptake from modified and unmodified tea waste $ Q\_{e}=\frac{\left(c\_{i}-c\_{o}\right)V}{M}$………………………………………………………………….2.1

where Ci and Ce are the initials and equilibrium metal concentrations, and qe is the metal absorption (mg metal adsorbed per g adsorbent). M is the mass of the dried adsorbent utilized, and V is the reaction mixture's volume (Kamau et al., 2020).
Pb (II), Cd (II), and Cu (II) removal percentages (R%) in solution were calculated.

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

Where Co and Ce are the initial and equilibrium metal concentrations.

The significance of the data was ascertained using statistical analysis employing ANOVA.

**3. RESULTS AND DISCUSSION**

The adsorbents' surface appearance and texture were assessed using SEM, and the functional groups responsible for adsorption were examined using FTIR. The effects of the initial metal ion concentration, pH of the solution, contact time, and adsorbent dosage were examined. The findings were presented as the removal effectiveness (% Removal) of the adsorbent. Analyzing the cadmium ion on adsorption onto acid-treated and raw tea waste the result reveals that treating natural tea waste with sulfuric acid enhances their surface ligand binding sites and, consequently, their adsorption efficiency.

**3.1 Surface characterization of biomass tea waste**

Figure 1 illustrates the surface appearance and texture of the tea waste adsorbent as shown in the SEM images. Figure 1 illustrates the tea waste's sluggish rough and restrictive surface before H2SO4 treatment. However, as can be observed in fig. 1(b), the biomass tea waste developed distinct pores following treatment with sulfuric acid. The partial breakdown of hemicellulose, cellulose, and lignin brought by sulfuric acid treatment may be the cause of the morphological changes in the biomass's structure. The adsorption capabilities of the acid-modified tea waste improved as a result of these morphological alterations. (Nthiga *et al.*, 2016). showed similar outcomes with acid-treated orange peel and avocado seed.



(a)



(b)

**Fig 1: SEM images for (a) UTW (b) MTW**

The existence of the isolated silanols was the cause of the weak absorption bands at Vmax 3885cm-1 for both MTW and UTW (Huang Ma and Zhao (2015). It indicates that the significant absorption bands at Vmax 3392cm-1 of UTW and 3392cm-1 of MTW, respectively, were caused by the hydroxyl groups' stretching vibration. For both MTW and UTW the existence of C=O stretching vibrations was the origin of the absorption band at Vmax 1645 cm-1. (Sych *et al.,* 2012).

The amine group stretching vibrations were suggested by the peak at Vmax1552cm-1 for both MTW and UMT. Both MTW, and the peaks seen at 1413 cm-l ascribed to the –COO-l groups (Nikhil and Bhalerao, 2019). For both modified and unmodified tea waste, the band at Vmax1255 cm-1 was connected to the hydrogen-bonded P-O and O-C stretching mode, which are seen in P-O-C and P-OOH. The chemical modification may be the cause of the new peak's emergence at 1106 cm-1 (Godlewska *et al.,*2018. The peaks' shifting indicates how the metal ions and the hydroxyl group on the on the biomass's surface interact chemically (Nthiga *et a l*.,2016). The ionized linkage P-O- which was present in esters and phosphate was linked to the band at Vmax 1106 cm-l for acid-treated tea waste. It was also attributed to symmetric vibration in P-O-P. While the peak at Vmax 753cm-l was linked to in-plane ring deformation



 **Fig 2: FTIR spectra of unmodified and modified tea waste adsorbent**

**3.2 Optimization experiments**

**3.2.1 Effect of pH**

The pH of the solution affects the chemistry of the solution and the surface properties of the adsorbent in removal of heavy metals. Figure 3 shows how pH affects the percentage of cadmium ions removed. By raising the pH of the solution from 2 to 6, the adsorption of cadmium on the MTW and UMTW considerably increases. The percentage of metal ion removal arise between pH 2 and pH 6, after which it started to fall. The result show that UTW had a maximum sorption of pH 5.9 while MTW had a maximum adsorption of pH 6.0. Maximum adsorption at pH 4.5 was reported in raw and acid-treated maize tassel (Signh *et al.,* 2012). Adsorption at pH 4.2 and pH 6.1 (Mwangi *et al*., 2012).

The percentage removal of Cd (ll) ions increased to a maximum of pH 5.9 and 6.0. Further pH increases resulted in a decrease in adsorption in both MTW and UTW. At low pH, the protonation of the functional groups is closely related to the adsorbent's surface. The formation of cadmium hydroxide starts when the pH rises over 6.0. This prevents the ions of the metal from circulating and renders them unavailable for the purpose of adsorption. Precipitation affects the adsorption process. The result is also in line with earlier adsorption research that found a pH range of 4 to 5 pH for Cd (ll) ions removal by a variety of adsorbents (Samadi *et al.,* 2014).

**Fig 3: Effect of pH on adsorption of Cd2+ on UTW and MTW**

**3.2.2 Effect of contact time**

 At first, the adsorption of Cd2+ increased quickly up to equilibrium time for both MTW and UMT. The elimination percentage was almost steady this time signifying the achievement of equilibrium conditions, as seen in figure 4. It shows that for both MTW and UTW the maximum adsorption of 75.2% was reached in the first 85 minutes and 96% in the 95 minutes. The agitation time measured in this study compared to that which Benard and Jimoh (2013) reported using orange peel, but it is comparable to that which was disclosed by (Banarjee *et al*., 2012) on the investigation of Lead (II) ions adsorption by the peel of a watermelon. this is explained by variations in the adsorbent's nature and experimental conditions and procedures.

**Fig 4: Effect of contact time** **on adsorption of Cd2+ on UTW and MTW**

**3.2.3 Effect of adsorbent dosage**

The effect of adsorbent dosage on removal of Cd2+ ions was conducted and the results recorded in figure 5. The findings demonstrate that the dosage of the adsorbent affected the absorption of cadmium (II) ions. When the mass of the adsorbent rises, the uptake of cadmium (II) ions increases as well, reaching a maximum of 84.3% and 93.5% for UTW and MTW, respectively. The improved surface texture and micropore structure following acid modification were responsible for the observed increase in percentage removal, increasing the ability of the ions to enter the adsorption sites (Anwar *et al.,* 2010).

**Fig 5: Effect of mass of the biomass on adsorption of Cd2+ onto UTW and MTW**

**3.2.4 Effect of initial metal ion concentration**

 Fig 6 illustrates the considerable impact of the initial concentration of metal ions in aqueous solution on the adsorption of ions on UTW and MTW.The findings indicate that the absorption of Cd ions was lower in UMW than in MTW. This demonstrates that the acid treatment improved the metal ion sorption up to a maximum of 98.2 % for MTW and 97% for UTW. The profile of Cd2+ sorption was shown to rise as the initial metal concentration increased This is because increment in Cd (II) ions concentration is the driving force to be able to overcome mass transfer resistance between the aqueous solution and the superficial layer of the modified and unmodified tea waste Wasewar, 2010. This work yielded higher result than a study on the adsorption of copper (II) ions using raw banana peel, which found 88% at 10 mg/L, 5 g (Hossain *et al.*, 2012). The computed value of F was higher than the critical value, according to the results of the ANOVA test. As a result, this demonstrated that the mean at various initial metal ion concentration values differed significantly.

 **Fig 6: Initial Cd2+ ions concentration on adsorption by UTW and MTW**

**3.3 Adsorption isotherms**

In order to evaluate the adsorption capacity of an adsorbent, two important adsorption isotherm models. The Langmuir and Freundlich isotherm models were selected for this study in order to fit the experimental data. Equilibrium adsorption isotherms are defined by a particular constant whose value expresses the surface characteristics and affinity of the adsorbent for various contaminants (Darson et al., 2005).

**3.3.1 The Langmuir isotherm model**

The Langmuir isotherm postulates or implies that monolayer sorption, in which adsorbed molecules do not interact, takes place on a homogeneous surface. It goes on to explain that no more sorption may occur at a spot once it has been filled. This indicates that where maximal adsorption occurs, the surface will get saturated, preventing additional processes. The following equation represents this model; (Kamau et al., 2020)

$q\_{e}=\frac{Q\_{e}bc\_{e}}{1+bc\_{e}}$*……………………………………………………………………………2.2*

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

Where; qe represents the metal ion absorbed per gram of the adsorbent at equilibrium (mg/g) qmax represents the maximum metal bio sorption capacity b is the affinity constant for binding site ce equilibrium concentration of the adsorbate

**3.3.2 The Freundlich isotherm model**

The results will be compared to Freundlich isotherm in order to study the empirical relationship and will be applied onto heterogenous surfaces involving multilayer sorption. According to this model stronger binding sites will occupy first (Shamsuddin et al 2016). As more sites are occupying binding strength becomes weaker. The model is described by the following equation (Jafari and Senobari, 2012).

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

The equation can be linearized and the dependent constants kf and n can be found by linear regression

$ In qe = In k\_{f}+ \frac{1}{n}C\_{e}$……………………………………………………………………………2.5

where Ce: concentration of metal ions (mg/L) at equilibrium, qe: amount of metal ions removed (mg/g) at equilibrium. kf is adsorption capacity and n is adsorption intensity. The values of kf and n were calculated by plotting a graph of lnqe against lnce (Moyo et al., 2013; Nthiga et al., 2016).

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

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| **Langmuir** | **Freundlich** |
| **Adsorbent** | **qmax (mg/g)** | ***b*(L/mg)** | **R2** | **KF** | **1/n** | **R2** |
| UTW | 5.359 | 0.034 | 0.9647 | 1.286 | 0.2294 | 0.9641 |
| MTW | 6.7159 | 0.1147 | 0.9661 | 1.244 | 0.178 | 0.9654 |

This study analyzed the equilibrium data obtained from adsorption of Cd (II) onto raw powdered and acid treated tea waste using the Langmuir and Freundlich isotherms and results recorded in table 1. Correlation coefficients 0.9961 and 0.9647 show that the experimental data on the adsorption of Cd (II) onto raw and acid treated tea waste fitted well in Langmuir model. Adsorption capacities for the MTW and UMT were 6.7159 and 5.359 mg/g respectively. The calculated values of' l/n were 0.2294 and 0.178 for UTW and MTW respectively, indicating favorable sorption of Cd (ll) ions onto raw and acid treated watermelon peels (Achak et al., 2009). Lower values of b « 1) were noticed from the all the adsorption processes which indicates the high affinity of the adsorbent for Cadmium (kamau et al., 2020)

**Figure 7**: **Adsorption isotherm for Cd(ll) ions using modified tea waste (Langmuir isotherm)**

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**Figure 8** **Adsorption isotherm for Cd (ll) ions using modified tea waste (Freundlich isotherm)**

**Figure 9a: Adsorption isotherm for Cd (ll) ions using unmodified tea waste (Langmuir isotherm)**

**Figure 9b: Adsorption isotherm for Cd (ll) ions using unmodified tea waste (Freundlich isotherm)**

**CONCLUSION**

According to the results the following conclusion can be deduced.

1. Sulfuric acid was used to chemically modify biomass tea waste and there was Increase in the number of functional groups for Cd2+ ion adsorption. This was revealed by the FTIR spectra.
2. The biomass tea waste developed distinct pores following treatment with sulfuric acid. The partial breakdown of hemicellulose, cellulose, and lignin brought by sulfuric acid treatment may be the cause of the morphological changes in the structure and surface of the adsorbent.
3. Adsorbent dosage, contact time, pH, and initial metal ion concentration all had a significant effect on the adsorption process.
4. MTW displayed highest percentage removal for all the parameters under investigation.
5. Adsorption of Cd (II) onto both MTW and UTW was well described by Langmuir adsorption models as compared to Freundrich model.

**DISCLAIMER**

Author(s) hereby declare that no generative AI technologies and text-to-image generators have been used during the writing or editing of this manuscript. Additionally, the research was financed by the authors' own efforts.

Competing interests

According to the authors, there aren't any competing interests.

**CONTRIBUTIONS OF THE AUTHORS**

All of the authors worked together to complete this work. The study's design, statistical analysis and initial paper preparation were all completed by author PN. The study's analyses, literature searches, and research supervision were overseen by authors JK, AO and SM. The final manuscript was read and approved by all writers.

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**APPENDICES**

## **Appendix 1: Variation (ANOVA) for the effects of pH for Cd (II) ions removal**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source of variation  | Sum of squares | Degrees of freedom | Mean squared  | F-Calculated | P-Value | F- Critical |
| **Between Groups** | **178.846** | **1** | **163.837** | **85.48** | **1.8E-10** |  |
| **Within Groups** | **63.395** | **36** | **19.167** |  |  | **4.11** |
| Total | 242.2412 | 37 |  |  |  |  |

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

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source of variation  | Sum of squares | Degrees of freedom | Mean squared | F- Calculated | P-Value | F- Critical |
| **Between Groups** | 1.8986 | 1 | 1.8986 | 54.87 | 1.3-08 |  |
| **Within Groups** | 0.9345 | 35 | 0.0346 |  |  | 4.12 |
| Total | 2.8331 | 36 |  |  |  |  |

## **\**

## **Appendix 3: Variation (ANOVA) for the effect of contact time on Cd (ll) ions removal**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source of variation  | Sum of squares | Degrees of freedom | Mean squared | F- Calculated | P-Value | F- Critical |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Between Groups | 28076 | 1 | 28076 | 65.7 | 1.7-10 |  |
| **Within Groups** | **9768.345** | **41** | **427.3416** |  |  | **4.07** |
| Total | 37844.345 | 42 |  |  |  |  |

## **Appendix 4: Variation (ANOVA) for the effect of initial metal ion concentration on Cd (ll) ions removal**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source of variation  | Sum of squares | Degrees of freedom | Mean squared | F- Calculated | P-Value | F- Critical |
| Between Groups | 1472.34 | 1 | 1472.348 | 80.256 | 2.4-10 |  |
| Within Groups | 698.578 | 32 | 18.3456 |  |  | 4.15 |
| Total | 2170.926 | 33 |  |  |  |  |