

Using Cilantro (*Coriandrum Sativum*) to Remove Cadmium from Contaminated Water

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Abstract Accessibility to safe drinking water poses great risks to human health since heavy metal ions can accumulate their amounts along the food chain. Methods already in use for cleaning contaminated water have resulted in generating toxic sludge and are expensive. Cilantro leaves has been used to reduce the contamination of heavy metals like lead, mercury and copper in rod shellfish as contains bioactive components of flavonoids, saponines and fibers which are capable of absorbing heavy metal ions by chelating action. However, the most effective part of cilantro and the most effective form i.e. when green or dry has not been reported. Consequently, the present study aimed at investigating adsorption of Cd^{2+} ions by fresh and dry cilantro leaves and stems from simulated water. Cilantro fresh leaves and fresh stems were grounded to obtain the wet adsorbents while for the dry adsorbents, fresh cilantro leaves and stems were sun dried at room temperature until their weighed dry masses remained constant and grounded to fine powder. Batch sorption studies were carried out while varying parameters of contact time, shaking speed, temperature, adsorbent dose, pH and initial concentration of metal ions in solution. Residue Cd^{2+} ions concentrations were determined using atomic adsorption spectroscopy (AAS). The adsorption of Cd^{2+} ions was described by Langmuir isotherm with Q_{max} values of 250.00, 51.28, 4.68 and 15.06 mg/g for fresh leaves (FL), fresh stems (FS), dry leaves (DL) and dry stems (DS) biomasses respectively. The results from this study suggest that fresh and dry cilantro leaves and stems are potential adsorbents of Cd^{2+} ions.

Keywords Cilantro, Cadmium, Adsorption capacity

1. Introduction

The world population is ever-increasing causing rapidly industrialization leading to more demand for the dwindling water resources, making it precious in many more countries. Indeed, a new report from the World Bank indicates that water pollution threatens nearly all the globally agreed sustainable development goals (World Bank Group, 2019).

For many decades, the problem of water shortage has proved to be a serious issue affecting Kenya caused by years of repeated droughts, poor water supplies management, pollution of water and a huge increase in demand as the population increase (Marshall, 2011). Majority of the metals ions bio-accumulate and hence becoming a threat to human life. The direct deposition of heavy metals ions invested waste in water bodies needs to be checked to minimize the environmental degradation (Khan *et al.*, 2008). Some of the heavy metals ions include: nickel, cerium, iron, uranium, bismuth, antimony, chromium, gold, copper, cobalt, gallium,

zinc, platinum, uranium, thallium, tin, tellurium, vanadium and manganese (Fernández-luqueño *et al.*, 2013). The introduction of vast quantities of wastewater contaminated with heavy metal ions which when ingested above the permitted level, they may cause severe health problems (Barakat, 2011). Heavy metals soluble compounds in aqueous water bodies is a major problem because of their harmful nature on the living things in the water bodies (Gupta and Rastogi, 2008). Cadmium, which is used in battery manufacture, paints, plastic industry and electroplating is a known toxic metal. All heavy metals occur in surface waters and in particulate, dissolved phases as well as in colloidal, though dissolved concentrations are usually low. The heavy metal compounds solubility in surface waters is controlled by the water pH, the type and amount of ligands on which the metal could adsorb the redox environment of the system and the oxidation state of the mineral constituents (Kennish, 1992).

Developing research on a different treatment methods for example; membrane processes, coagulation, precipitation, sedimentation, filtration, flotation, biological methods, chemical processes, electrochemical method ion exchange and adsorption; with various degree of successes leads to elevated dramatic outcomes in the scientific world. However,

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these methods are expensive for use in developing countries, especially in rural areas. Consequently, there has been an urgent need to find modern technologies or bio-materials to rid heavy metal ions from contaminated water and biosorption is a promising option (Gupta and Rastogi, 2008). Biosorption uses biological materials capability to hold metal ions in contaminated water by either physicochemical or metabolically associated pathways for the uptake (Gupta and Rastogi, 2008). The major benefits of biosorption as opposed to conventional methods are that it is cheap and efficient, possible regeneration of sorbent, no additional nutrients is required, and possible metal recovery (Zhao *et al.*, 2011). Some biosorption studies use special isolated strains, locally available biomass while others use processed raw materials to increase their biosorption ability (Volesky and Holan, 1995). Large amount of waste substances of organic origin such as dead leaves, seed shells, barks, sawdust, roots and oil cakes from numerous plants in their powder form have found their use in the elimination of heavy metals ions.

Cilantro (*Coriandrum sativum*) mostly referred as Coriander or dhania is an annual plant of parsley family (Apiaceae) within order Apiales, is natural to the Mediterranean area and is widely grown in Russia, India, Central Europe, Bangladesh, and Morocco (Nazrul *et al.*, 2009). Cilantro has both medicinal and nutritional properties. It contains several active ingredients, primarily monoterpenes, limonene, α -pinene, p-cymene, γ -terpinene, citronellol, borneol, camphor, coriandrin, geraniol, dihydrocoriandrin, flavonoids coriandrins A-E, and essential oils. Cilantro has been shown to have many pharmacological effects like antifertility, digestive stimulant, antihyperlipidemic, antihyperglycemic, antioxidant, hypotensive and antiproliferative. Coriander is also utilized in detox diet (Leena *et al.*, 2012). Cilantro can be cultivated commercially or in small scale in kitchen gardens, flower pots and planting bags within homesteads. It is readily available, inexpensive and has shown promise in eradicating certain metals ions, for instance copper, mercury and lead that can be dangerous to human health (Ravichandran, 2011). In another study, several natural substances were found to chelate given heavy metal ions while others did not. However, only one compound-HMD (Heavy Metal Detox)-tested in double blind, placebo controlled tests was found to be effective in mobilizing and excreting metals in the faeces and urine for all the metals experimented. HMD consists of a homeopathic homaccord of cell decimated *Chlorella*, (*Cilantro*) *Coriandrum sativum* leaf tincture and *Chlorella* Growth Factor was found to be a synergistic powerful chelating formula which was cost effective (George, 2005). Therefore the study aims at investigating on the ability of cilantro biomass efficiency and capacity to remove cadmium metal ions dissolved in water through adsorption.

Adsorption is a surface process in which multi-component fluids are attached to the surface(s) of a solid adsorbent(s),

forming chemical or physical bonds. It is being recognized as one of the widely applied and most efficient fundamental approach in contaminated water treatment methods which mainly revolves on its technical feasibility, economical viability, socially acceptable and simplicity (Foo and Hameed, 2010). The interaction between some metal ions adsorbed onto the adsorbents surfaces and the metal ions concentration in the solution at equilibrium conditions can be expressed by adsorption isotherms (Reddy *et al.*, 2014). There are many isotherm equations for adsorption but the two mainly applied are the Freundlich and Langmuir isotherms (Katircioğlu *et al.*, 2008). Langmuir isotherm represents equilibrium distribution of adsorbate between the liquid and solid phases. The model is applicable for the monolayer sorption onto a surface which contains a fixed number of equal sites. The Langmuir isotherm assumes a uniform dynamism of adsorption onto the surface and no migration of adsorbate on the plane of the surface (State and State, 2012). The model views every adsorption site as energetically equivalent and identical i.e. thermodynamically, every location can hold only one adsorbate molecule (Al-anber, 2011). The linear form of Langmuir adsorption isotherm is shown by the given equation (Katircioğlu *et al.*, 2008);

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{bQ_{max}} + \frac{C_{eq}}{Q_{max}} \quad (1)$$

where, C_{eq} denotes the metal ions concentration in solution in mg/L at equilibrium, Q_{eq} represent the quantity of metal ions adsorbed per gram of adsorbent at equilibrium (mg/g) and 'b' is the Langmuir isotherm affinity constant and it is associated with adsorption energy in L/mg. Q_{max} represents adsorbents' adsorption capacity in mg/g. From the linearized form of the langmuir isotherm, a plot of C_{eq}/q_{eq} versus C_{eq} , the constants 'b' and Q_{max} can be calculated using the graph's slope and the intercept (Katircioğlu *et al.*, 2008). Freundlich adsorption isotherm has been viewed as an empirical relationship and it has been mostly used to fit experimental data (State and State, 2012). A linear form of the Freundlich isotherm is given by the equation (Jafari and Senobari, 2012);

$$\text{Log}(Q_e) = \text{log}(K_f) + \frac{1 \text{log}(C_e)}{n} \quad (2)$$

Where, K_f and 'n' represents the Freundlich isotherm constants indicating the adsorption capacity and intensity respectively, Q_e is the adsorption density and C_e amounting to the metal ions concentration at equilibrium. When $\text{log } Q_e$ is plotted versus $\text{log } C_e$, $\text{log } K_f$ is the y-intercept and '1/n' is the gradient of the linear line (Coles and Yong, 2006). The Freundlich constant '1/n' is a factor of the power of adsorption during process. When $n = 1$, the partition between the two phases are independent of the concentration. If the value of '1/n' is less than one it show a standard adsorption (State and State, 2012). The slope is between 0 and 1 which measures the surface heterogeneity or adsorption intensity. The surface become extra heterogeneous as it tends to 0.

2. Materials and Methods

Cilantro samples were bought at Githurai market in Kiambu County where there is continuous supply throughout the year. The sample was identified by a plant taxonomist at plant science department in Kenyatta University. The sample was deposited at Plant Science Department Hebanum at Kenyatta University. The biomass was taken to Kenyatta University chemistry laboratory where it was thoroughly washed using distilled water to get rid of soil and dust particles. For the wet biomass, the fresh leaves and stems were chopped 1cm and then grounded to increase the surface area for adsorption. For the dry biomass, fresh cilantro stems and leaves were sun dried at room temperature until the weighed dry masses remained constant to ensure that negligible moisture content was in the samples. The dry samples were then cut and grounded to fine powder. The moisture content was calculated by the difference between the wet and dry sample masses.

Chemicals and Reagents: Analytical grade $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ of molecular mass 308.47 with 99.0% purity salts obtained from Sigma Aldrich Company was used for the preparation of the stock solutions of Cd^{2+} ions. Stock solution containing 1000 mg/L of Cd^{2+} ions was made by diluting 2.754 g $\text{Cd}(\text{NO}_3)_2$ in 1000 mL of distilled water in 1000 mL volumetric flask. A working solution of 100 mg/L of Cd^{2+} ions was prepared by diluting 100 mL of Cd^{2+} ions of stock solution to 1000 mL using distilled water in a 1000 mL volumetric flask. Standard solution of 2, 4, 6, 8 and 10 mg/L of Cd^{2+} ions was prepared by diluting 2, 4, 6, 8 and 10 mL respectively of the 100 mg/L working solution in a 100 mL volumetric flask using distilled water. 1.0 M of Standard HCl acid with 71.0% purity was prepared by diluting 68 mL of the acid and diluting it to 1000 mL with distilled water. 1.0 M NaOH base solution of molecular weight 40 from Merck Limited (India) was prepared by diluting 40 g of NaOH salt in 1000 mL distilled water. 1.0 M of NaOH and 1.0 M of HCl were used for pH adjustments during the batch adsorption studies.

Instrumentation: Residue Cd^{2+} ions concentration in the various solutions were determined using AAS (Buck Scientific 210 HZ 50-60; USA), at wavelength of 228.8 nm in flame mode using air-acetylene flame. Standard and blank samples were run after every ten samples to check the AAS instrumental drift. The pH meter PHEP, Hanna Instrument from Italy was used to measure the pH in this study at a temperature of 25.0°C. Turbid Meter (2100P HACH) was used to determine the turbidity of water. Fourier transform infra-red machine (Perkin Elmer 100, Waltham Ma; USA) was used to deduce the main functional groups of dry cilantro leaves and stems. Calibration curve method was used to quantify the heavy metal ions concentration.

Statistical Testing: The data from the study was treated by Analysis of variance (ANOVA) and Student Newman-Keuls (SNK) test for significance. Mean values that are followed by the same superscript letter (s) i.e. a, b, c and d within the same row do not differ significantly at 95% confidence level

otherwise they differ significantly as SNK-test in tables for the percentage removal in appendices 2 (Kothari, 2004).

Batch Experiments: The batch parameters under the study were initial metal ions concentration, dosage, pH, shaking speed, temperature and contact time on adsorption. The quantity of Cd^{2+} ions adsorbed per unit mass of the adsorbents and their percentage removed were evaluated using the equations 3 and 4 respectively;

$$q_e = \frac{(C_o - C_e)}{m} V \quad (3)$$

$$R = 100 \left(\frac{C_o - C_e}{C_o} \right) \quad (4)$$

where,

C_o is the initial concentration of sorbate.

q_e is the amount of sorbate adsorbed per unit mass of adsorbent at equilibrium.

C_e is the concentration of sorbate at equilibrium.

m is the mass of sorbent used in grams.

V = volume of solution in litres.

R = percentage removal.

The percentage removal of adsorbate were calculated as the ratio of the difference in adsorbate concentration before and after adsorption ($C_o - C_e$) to the initial concentration of the adsorbate of the aqueous solution expressed as a percentage (Apiratikul and Pavasant, 2008). The optimum values were determined by taking the highest percentage amount of metal ions adsorbed per unit mass of the adsorbent for each batch experiment.

Effect of Initial pH on the Adsorption of Cd^{2+} Ions: The influence of pH on adsorption of the metal ions was studied at pH 2, pH 5, pH 7, pH 8, and pH 9. The pH adjustment of all the samples was achieved by using a filter paper strip soaked in 0.1 M HNO_3 and 0.1 M NaOH solutions accordingly (Al-Degs *et al.*, 2008). At each pH, 0.2 g of adsorbents was shaken in 50 mL of the 100 mg/L Cd^{2+} ions solutions. All sampling test were conducted in triplicates and were shaken for 2 hours in a water bath shaker at constant speed of 6 rps at a temperature of 25°C.

Effect of Adsorbent Dosage on the Adsorption of Cd^{2+} Ions: The effect of altering the adsorbent dosage on the adsorption of Cd^{2+} ions was studied by shaking 50 mL of Cd^{2+} ions solutions in triplicate with various dosages of 0.1, 0.2, 0.5, 1.0 and 2.0 g. Initial concentrations of the aqueous metal ions solution was kept constant at 100 mg/L at a pH 6. The experiment was conducted in triplicates and agitated for 2 hours in the water bath shaker. The samples were filtered using Whatman No.1 and the filtrates were measured for residual Cd^{2+} ions concentration using AAS.

Effect of Contact Time on the Adsorption of Cd^{2+} onto the Adsorbents: The effect of contact time on the adsorbent was investigated by measuring 50 mL of 100 mg/L metal ions solution in a 120 mL plastic bottles and adding 0.2 g of biomass. The pH of the sample was adjusted to 6 and shaken at 6 rps for the time ranging from 30 minutes to 3 hours. The solution was filtered and the filtrates were subjected to AAS to record the absorbance of the residue metal ions.

Effect of Initial Metal Ions Concentration on the Adsorption of Cd²⁺ ions on to Adsorbents: Initial metal ions concentration was investigated by agitating 50 mL of metal ions solutions of 20, 50, 100, 200, 300, 500, 800, and 1000 mg/L of Cd²⁺ ions in 120 mL plastic containers with 0.2 g of the adsorbents in a water bath shaker at 25°C. The bottles were shaken at pH of 6, a shaking speed of 6 rps for 2 hours. The residual Cd²⁺ ions concentration was measured with AAS machine. All sampling tests were conducted in triplicate.

Effect of Shaking Speed on Adsorption of Cd²⁺ Ions: 0.2 g of each adsorbent was added to 120 mL stoppered plastic bottles containing 50 mL of 100 mg/L Cd²⁺ ions solutions. The pH of each sample solution was adjusted to 6.

The bottles were shaken in a water bath temperature controlled shaker at 25°C at different speeds of 2, 4, 6, 8, and 10 rps at a contact time of 2 hrs. The solution was filtered and the filtrates subjected to AAS to record absorbance of the residue metal ions concentrations.

3. Results and Discussion

Functional Group Analysis of Cilantro: Fourier transform infra-red (FTIR) spectroscopy was used to deduce the main functional groups in cilantro biomass of dry leaves (DL) and dry stems (DS). The IR spectrum of cilantro biomass is given in figure 1.

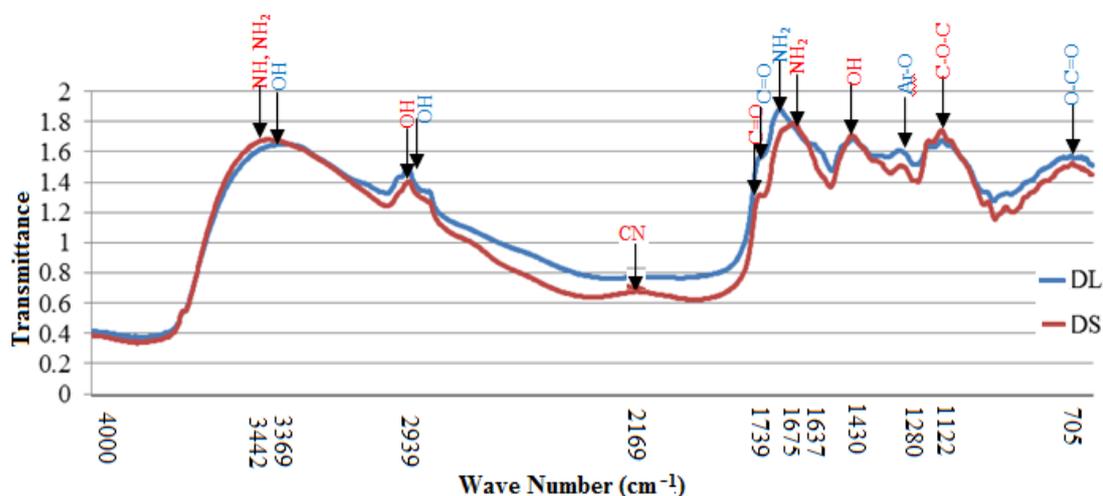


Figure 1. FTIR spectrum of Dry Leaves (DL) and Dry Stems (DS)

Adsorption of metallic ions is favoured by different chemical functional groups. They are potential active sites for the uptake of metal ions depending on factors like their accessibility, abundance of the sites, chemical states, attraction between the metal ions and adsorption sites (Jafari and Senobari, 2012). The FTIR spectra for DS was a broad peak at 3442 cm⁻¹ representing a -NH and -NH₂ stretching vibrations in aromatic amines while a broad peak at 3369 cm⁻¹ suggested a -OH stretching vibrations in alcohols and phenols for DL with a -OH stretching vibrations band at 2937 cm⁻¹ in carboxylic acid for DS and DL (Jafari and Senobari, 2012). The band at 2169 cm⁻¹ showed a -CN stretching in thiocyanates for DS. The band at 1739 cm⁻¹ represents -C=O symmetric stretching vibration in hydride for both DS and DL, and a -NH₂ bending at 1637 cm⁻¹ in primary amides for DS (Gupta and Rastogi, 2008). A band at 1675 cm⁻¹ represents a -NH₂ in primary amines for DL. The band at 1430 cm⁻¹ represent a -OH in-plane bending in carboxylic acid and a -C-O-C band at 1122 cm⁻¹ which represent antisymmetric stretching vibration for DS. The band at 1280 cm⁻¹ represents a Ar-O stretch in alkyl and aryl ether while a -O-C=O bending vibrations in carboxylic acid for DL was observed at 705 cm⁻¹ as also reported by (Singh and Kaur, 2013).

Effect of pH on the Adsorption of Cd²⁺ Ions: Metal ions adsorption is normally influenced by the nature of the adsorbents surfaces and the heavy metal ions species distribution. Surface distribution is mostly controlled by the system pH (Senthil *et al.*, 2010). The pH effect was investigated by determining the percentage of Cd²⁺ ions removed as pH was altered from 2 to 9 while keeping all other conditions and parameters same. The percentage removal of Cd²⁺ ions with variation in pH were fitted in figures 2.

The percentage removal of Cd²⁺ ions was influenced by the ionic strength of the solution. From figure 2 it is clear that, between pH 5 and pH 8, there were higher values of percentage removal of Cd²⁺ ions. The percentage removal was 80.5% for FL, 80.2% for FS, 81.0% for DL and 82.1% for DS at pH 2. The percentage removal at pH 9 was 83.8%, 82.9%, 84.3% and 84.7% for FL, FS, DL and DS respectively. The highest percentage removal for Cd²⁺ ions was 83.8% at pH 8 for FL, 83.2% at pH 7 for FS, 85.9% at pH 8 for DL and 87.2% at pH 8 for DS. The pH of the system influences both the cell wall binding sites and the chemical nature of heavy metal ions in solution (Katircioğlu *et al.*, 2008). Lower acidic range causes the surface of the adsorbents to be protonated hence does not encourage the

uptake of Cd^{2+} ions species. Moreover, at lower pH range the surfaces of the adsorbents are associated with H^+ species thus hindering the accessibility of metal ions by repulsive forces of the surface functional groups, hence lowering the percent of heavy metal ions removal. However, the surface of the adsorbent becomes deprotonated in the alkaline range favouring the uptake of metal ions under restricted limitations because of hydrolysis (Das, 2012). The rapid increase in the adsorption between pH 2 to pH 6 shows an increase in electrostatic forces of attractions between the negatively charged binding sites and the positively charged metal ions (Katircioğlu *et al.*, 2008). Similar results were reported on studies on adsorption of Cu^{2+} from a solution by *Elais guineensis* kernel activated carbon (Tumin and Chuah, 2008).

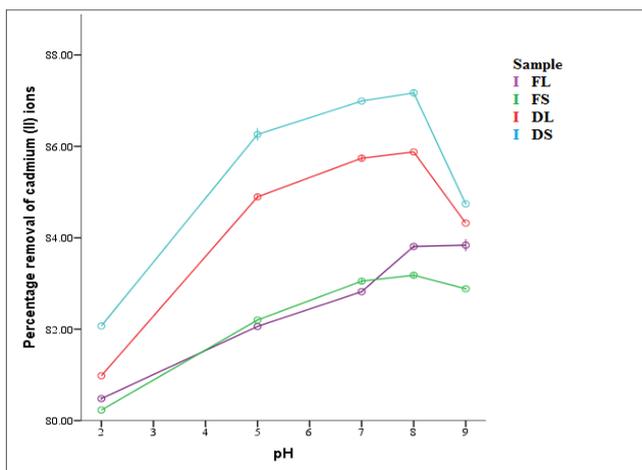


Figure 2. Effect of pH on percentage removal of Cd^{2+} ($T = 298 \text{ K}$, time = 2 hrs, concentration = 100 mg/L, dosage = 0.2 g, shaking speed = 6 rps)

Effect of Adsorbent Dose on the Adsorption of Cd^{2+} Ions: The influence of dosage is among effective factors in batch sorption studies. The effect of the adsorbent dose of fresh and dry cilantro leaves and stems was investigated by determining the percentage of Cd^{2+} ions removed as adsorbents amounts were varied from 0.1g to 2.0 g while keeping all other conditions and parameters the same. The percentage removal of Cd^{2+} ions varied with adsorbent doses as shown in figures 3.

Figure 3 indicates that the percentage of Cd^{2+} ions removal by FL increased from 81.1% to 83.7% when the adsorbent dosage was increased from 0.1g to 1.0g followed by a decrease to 82.1% at a dosage of 2.0 g. The FS percentage removal for Cd^{2+} ions increased steadily from 82.0% to 90.5% when the adsorbent dose was raised from 0.1 g to 2.0 g. The percentage removal of Cd^{2+} ions by the DL increased from 83.0% to 85.5%, while for the DS the percentage removal increased from 83.4% to 99.7% at dosage of 0.1g to 1.0g and a decreased to 88.7% at a dosage of 2.0g. The highest percentage removal efficiency of Cd^{2+} ions was 83.7% at 1.0 g for FL, 90.5% at 2.0 g for FS, 85.4% at a dosage of 2.0 g for DL and 99.7% at a 1.0 g for DS dosage. Figures 3 show that as the adsorbents dosage increases, it leads to increasing adsorption of the metal ions. When the

adsorbents dosage increases, the amount of active surface sites available for adsorption also increases (Edris *et al.*, 2012). Beyond the optimum dosage there was no significant variation in adsorption or lowering of percentage removed. This could be attributed to the overlap of adsorption surface sites due to overcrowding of the adsorbent particles. The results suggest that within certain range of initial metal ions concentrations, the percent of metal ions adsorbed onto the adsorbents is determined by their adsorption capacity (Senthil and Kirthika, 2009). The decrease in percentage of metal ions removal could be attributed to the concentration gradient between the adsorbent and the metal ions i.e. as the adsorbents concentration increase it leads to a decline in the amounts of metal ions adsorbed onto a unit weight of the biomass (Edris *et al.*, 2012). Moreover, higher adsorbents doses may cause shielding effects on the denser outer layers of the cell walls, thereby screening the binding sites from metal ions (Onundi *et al.*, 2010). Similar results were reported on study of adsorption of Cd^{2+} ions on activated carbon made from coconut shell (Devi *et al.*, 2012).

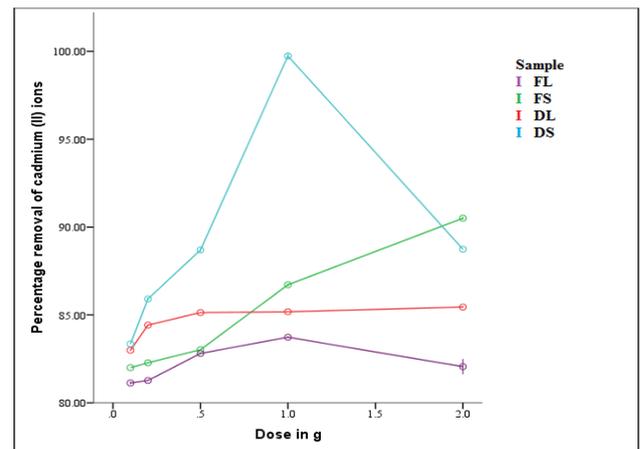


Figure 3. Effect of adsorbent dosage on percentage removal of Cd^{2+} ions ($T = 298 \text{ K}$, time = 2 hrs, concentration = 100 mg/L, pH = 6.0, shaking speed = 6 rps)

Effect of Contact Time on Adsorption Process on the Adsorption of Cd^{2+} Ions: The study of the effect of contact time on adsorption was investigated by determining the percentage of Cd^{2+} ions removed as time were varied from 30 to 180 minutes while keeping all other conditions and parameters same. The percentage removal of Cd^{2+} ions by FL, FS, DL and DS was presented on the figures 4.

Figure 4 it is shows that, the percentage removal of Cd^{2+} ions by DS increased as time progressed from 86.6% at thirty minutes to an optimum value of 87.3% at 2 hours. The percentage removal for Cd^{2+} ions was almost a plateau with a range from 81.3% to 81.33% for the FL as time increased from thirty minutes to three hours. The optimum percentage removal for DL was 85.33% at two hours while DS had an optimum of 86.98% after 3 hours. The percentage metal ions removal efficiencies increase with increasing contact time as there are plenty vacant surface sites before an equilibrium is reached (Argun *et al.*, 2007). After the rate of adsorption equaled the rate of desorption, there were no significant

changes in percentage of metal ions removal from the solution (Jeyakumar and Chandrasekaran, 2014). The large numbers of vacant surface sites once are occupied with time, it is difficult to occupy the vacant surface sites remaining as there are repulsive forces between the bulk in solution and the solute ions on the solid surface (Gulipalli *et al.*, 2011) hence desorption may occur as indicated by decrease in percentage removal at later time. Similar results were reported on studies of kinetics and thermodynamics of Cd^{2+} ions adsorption from solution onto rice husks (Senthil *et al.*, 2010).

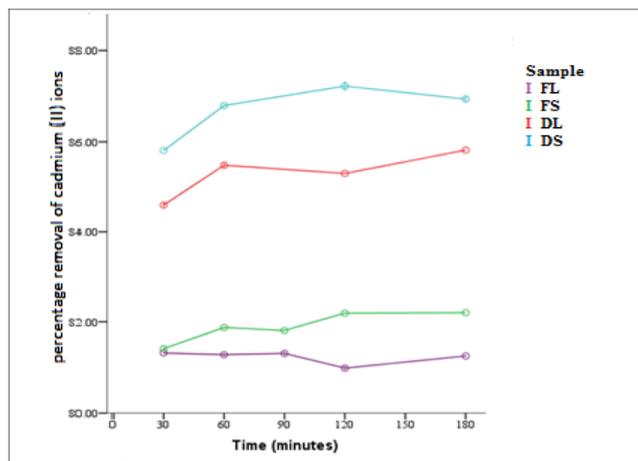


Figure 4. Effect of contact time on percentage removal of Cd^{2+} ($T = 298\text{ K}$, $\text{pH} = 6$, concentration 100 mg/L , dosage $= 0.2\text{ g}$, shaking speed $= 6\text{ rps}$)

Effect of Shaking Speed on Adsorption of Cd^{2+} Ions:

Shaking speed influences the efficiency of all the binding sites readily available for metal ions uptake (Anwar *et al.*, 2009). The study of the influence of shaking speed on adsorption uptake was done by determining the percentage removal of Cd^{2+} ions when the shaking speed was varied from 2 to 10 revolutions per second (rps) while keeping all other conditions and parameters the same. The percentage removal of Cd^{2+} ions by FL, FS, DL and DS was presented on the figures 5.

The percentage removal of Cd^{2+} ions increased with increase in shaking speed. From the figure 4, it is clear that there was almost a merge on percentage removal of Cd^{2+} ions by FL and FS with an optimum percent of 81.8% for FL and 81.7% for FS at 6 rps respectively. The percentage removal of Cd^{2+} ions by DL increased from 84.5% at 4 rps to an optimum of 85.3% at 10 rps. The highest percentage removal of Cd^{2+} ions by the DS was 86.5% at 10 rps. Figure 4 indicate that increasing the shaking speed leads to increased retention capacity of metal ions (Medjram and Ferroudj, 2013). This effect of decrease in the boundary layer thickness around the adsorbents particles result from increasing degree of mixing. As the mixture was shaken, the solute particles moved around rapidly in solution causing an increase in concentration of metals ions near the surfaces of the solute particles mostly near that of bulk concentration (Argun *et al.*, 2007). The metal ions diffusion rate to the boundary layer between the surrounding solution and the

adsorbents particles, increase with increasing shaking speed causes the speed of the external mass transfer of the metal ions to increase reaching equilibrium rapidly. However higher shaking speeds provide enough additional force to break the new formed bonds between the adsorbents surfaces and the metal ions (Argun *et al.*, 2007). Similar results were observed on adsorption study of Cd^{2+} ions on radish peels (Anwar *et al.*, 2009).

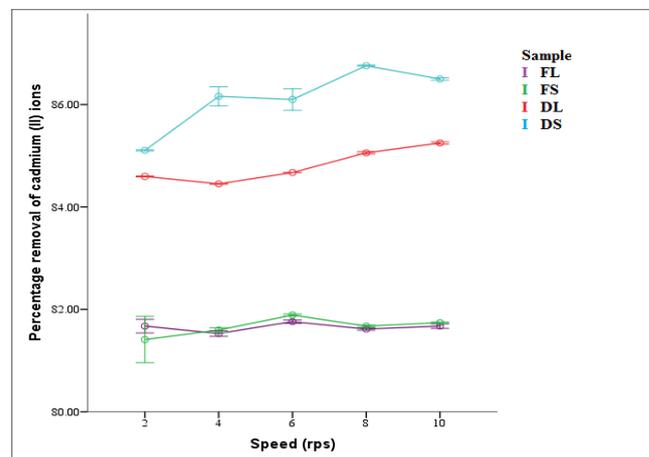


Figure 5. Effect of shaking speed on percentage removal of Cd^{2+} ($T = 298\text{ K}$, time $= 2\text{ hrs}$, concentration $= 100\text{ mg/L}$, dosage $= 0.2\text{ g}$, $\text{pH} = 6$)

Effect of Initial Metal ions Concentration on the Adsorption of Cd^{2+} Ions:

The study of the effect of metal ions concentrations on adsorption uptake was investigated by determining the percentage removal of Cd^{2+} ions as initial metal ions concentrations was varied from 20 to 1000 mg/L for Cd^{2+} ions. The percentage removal of Cd^{2+} ions by FL, FS, DL and DS was represented on the figures 6.

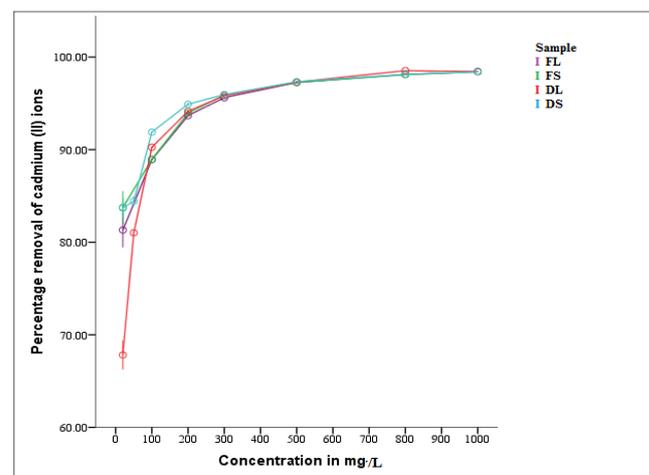


Figure 6. Effect of initial metal concentration on percentage removal of Cd^{2+} ($T = 298\text{ K}$, time $= 2\text{ hrs}$, shaking speed $= 6\text{ rps}$, dosage $= 0.2\text{ g}$, $\text{pH} = 6$)

From the figure 6, it is clear that increasing initial metal ions concentration increased the percentage removal of Cd^{2+} ions by all the adsorbents. At concentration of 20 mg/L the percentage removal by FL, FS, DL and DS rose from 81.3%, 83.8%, 67.8% and 83.7% and attained a plateau at 300 mg/L with 95.6%, 95.9%, 95.8% and 95.9% for FL, FS, DL and

DS. The percentage removal at 800 mg/L for Cd^{2+} was 98.1% for FL, 98.1% for FS, 98.5% for DL and 98.1% for DS. The quantity of metal ions adsorbed per unit mass of the adsorbent increases with the initial heavy metal ions concentration which may result from higher availability of heavy metal ions in the solution. Further higher initial concentration increases the driving force overcoming all mass transfer resistance of metal ions between the solid and aqueous phases hence a higher probability of collisions between adsorbents and the metal ions (Sen *et al.*, 2013). These can be explained as a result of gradual increase in the electrostatic interactions between the Cd^{2+} ions with the active sites in the adsorbents. Moreover, as the metal ions concentration in the solution increased, more active sites were being covered. Besides, higher initial concentration leads to an increase in the attraction of the metal ions towards the active sites. The decrease in the adsorption capacity at higher concentrations could be seen as smaller number of vacant sites were available on the adsorbents versus a higher number of the sorbents at the higher concentrations (Tumin and Chuah, 2008). Similar results were obtained on kinetic and thermodynamic studies of Cd^{2+} ions adsorption from a solution onto rice husks (Senthil *et al.*, 2010).

Effect of Temperature Changes on the Adsorption of Cd^{2+} Ions: Temperature affects the rate of diffusion of sorbate onto the sorbents surface. The study of how the temperature affect adsorption uptake was investigated by determining the percentage of Cd^{2+} removed as the temperature was raised from 298K to 323K while keeping all other conditions and parameters the same. The percentage removal of Cd^{2+} ions by FL, FS, DL and DS was represented on the figures 7.

Figure 7 indicates that the percentage removal of Cd^{2+} ions using DL and DS at 298K increased gradually from 83.9% for DL and 86.2% DS for to 84.7% for DL and 87.1% for DS at 308K then an increase to 91.4% and 91.5% at 323K respectively. FL and FS maintained a plateau from 298K to 308K for Cd^{2+} ions with an increase in percentage removal from 82.1% and 84.1% at 308K to 85.8% and 85.9% at 323K respectively. The maximum percentage removal for Cd^{2+} ions was 85.8%, 85.9%, 91.4% and 91.5% for FL, FS, DL and DS respectively at 323 K. Adsorption of Cd^{2+} ions

increased as the temperature increased. Increase in temperature leads to increasing the rate of diffusion of given metal ions across internal pores and the external boundary layer of the adsorbents particles. Consequently, increase in temperature produces swelling effects within the internal structures of the cell walls facilitating large metal ions to further penetrate. The considerable increase in the number of Cd^{2+} ions adsorbed with rising temperatures shows an endothermic type of process (Zulfikar *et al.*, 2013). Similar results were reported on adsorption equilibrium and dynamics studies of Zn^{2+} ions onto chitosan (Karthikeyan *et al.*, 2004).

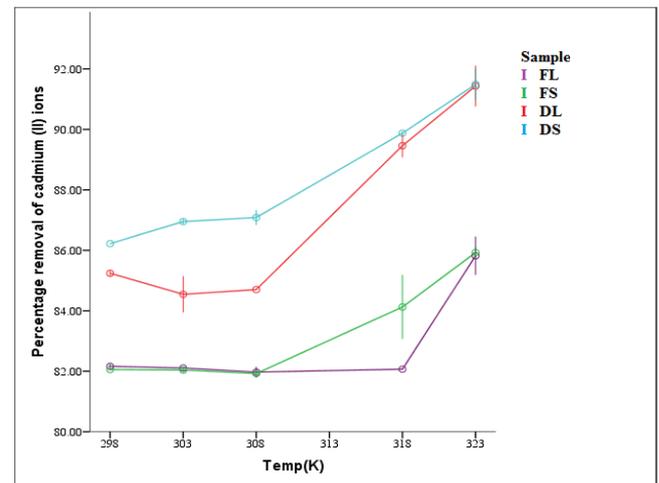


Figure 7. Effect of temperature on percentage removal of Cd^{2+} ions (time = 2 hrs, shaking speed = 6 rps, dosage = 0.2 g, pH = 6, concentration = 100 mg/L)

Adsorption Isotherm: In the study, Langmuir and Freundlich adsorption isotherms were used to demonstrate the relationship between the amounts of Cd^{2+} ions adsorbed at their equilibrium concentrations in solution. The analysis of the adsorption data by fitting it the isotherm models is a crucial step for finding a suitable model to be used for a design purpose (Muherei and Junin, 2009). The adsorption isotherms of Cd^{2+} ions are shown in figures A₁ to A₁₀ in appendices 1 and their thermodynamics parameters summarized in tables 1.

Table 1. Langmuir and Freundlich parameters for Cd^{2+} ions adsorption by FL, FS, DL and DS

Adsorbent	Cd^{2+} ions					
	Langmuir			Freundlich		
	Q_{\max} (mg/g)	b (L/mg)	r^2	K_f	1/n	r^2
Fresh Leaves (FL)	250.00	0.044	0.9911	1.72	2.377	0.9295
Fresh Stems (FS)	51.28	0.043	0.9990	2.17	2.170	0.9195
Dry Leaves (DL)	4.68	0.069	0.9224	0.0003	4.869	0.9653
Dry Stems (DS)	15.06	0.070	0.9591	0.29	2.209	0.9849

From the table 1, Cd^{2+} ions had adsorption affinity ('b') values of 0.044, 0.043, 0.069 and 0.070 L/g for FL, FS, DL and DS respectively for Langmuir isotherm. The K_f values of Cd^{2+} ions adsorption for the Freundlich isotherm were 1.72,

2.17, 0.0003 and 0.29 mg/g and 1/n values of 2.377, 2.170, 4.869 and 2.209 for fresh FL, FS, DL and DS respectively. The adsorption of Cd^{2+} ions was best fitted in Langmuir isotherm with adsorption capacity (Q_{\max}) values of 250.00,

51.28, 4.68 and 15.06 mg/g and correlation values (r^2) of 0.9911, 0.9990, 0.9224 and 0.9591 for FL, FS, DL and DS respectively. Despite high r^2 values of 0.9295, 0.9195, 0.9653 and 0.9849 in Freundlich isotherm for FL, FS, DL and DS respectively on adsorption of Cd^{2+} ions, the adsorption intensity ($1/n$) values for the Freundlich model were greater than 1 hence the adsorption was unfavorable for this model (Al-anber, 2011). According to Freundlich model, adsorption occurs on heterogeneous surfaces and active sites have different values of adsorption energy (Muherei and Junin, 2009). Similar results were reported on adsorption models for treatment of experimental data on removal F^- ions from water by oxihydroxides of Al (Zelentsov *et al.*, 2012) and also reported by the applicability of the Freundlich adsorption isotherm indicating that the adsorption by chitin may be governed by physisorption on adsorption studies of Fe^{3+} on chitin (Karthikeyan *et al.*, 2005).

4. Conclusions

The adsorption of Cd^{2+} ions was best explained by Langmuir adsorption isotherm with Q_{max} values of 250.00, 51.28, 4.68 and 15.06 mg/g for FL, FS, DL and DS respectively. The percentage removal efficiency values for FL and FS for Cd^{2+} ions for all the parameters under batch studies ought to be much higher, since 0.2 g of FL on drying gave 0.017 g dry biomass with a moisture content of 91.5%, while 0.2 g of DS on drying gave 0.1 g of dry biomass with moisture content of 50%; considering that all adsorbents dosage was maintained at 0.2 g during the batch adsorption studies.

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