

ADSORPTION CAPACITY OF CARBONIZED TITHONIA DIVERSIFOLIA TOWARDS Cd^{2+} AND Cu^{2+} UNDER DIFFERENT pH, ADSORPTION CAPACITY AND CONCENTRATION

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ABSTRACT

Adsorption studies were performed to investigate the adsorption capacity of carbonized *Tithonia diversifolia* towards heavy metal ions (Cd^{2+} and Cu^{2+}) under different pH, contact time, concentration and temperature conditions. Cadmium metal concentrations at; 25 ppm, 50 ppm, 75 ppm, 100 ppm, 150 ppm and 200 ppm of metal solutions were prepared and the pH was adjusted to 5. The uptake of copper (II) increases as the pH of the solution increases; at pH 1, pH 2, pH 3, pH 4 and pH 5, percentage metal bound were 20.59, 48.47, 94.26 and 94.08% respectively, at pH 5 and pH 6, percentage metal bound dropped to 93.26, 92.62% respectively. The increase in the removal of copper as pH increases is attributed to the decrease in competition between proton and Cu^{2+} ion for the surface site. Cadmium study showed that the optimum binding pH is 5 while at pH 1, pH 2, pH 3, pH 4 and pH 6, percentage bound were 25.59, 59.12, 96.76, 96.14 and 98.31% respectively. The percentage removal for cadmium (II) ion is low at pH 1 and remains high and almost constant at pH 6. The high binding power of cadmium (II) ion at the initial stage is attributed to the biomass having maximum binding sites available for interaction. Our findings showed that the amount of Cu^{2+} and Cd^{2+} adsorbed was found to vary with the initial solution pH, adsorbent dosage and concentration.

Keywords: Adsorption, Cadmium, Copper, Heavy Metals, *Tithonia diversifolia*

INTRODUCTION

Heavy Metals: Diverse amounts of heavy metals may be found everywhere; in soils, water, sediments, and plants, even in the Arctic [1]. The emission sources of these xenobiotics have been studied for several years to reduce pollution. Heavy metals once introduced to the environment by one method may spread to various environmental components, which may be caused by the nature of interactions occurring in this natural system. Heavy metals may chemically or physically interact with natural compounds,

which change their oxidation states and precipitate [2]. The exposure of terrestrial environment to heavy metals can come from a number of sources but pipeline leak are a major contributor. Although the state-of-the-art technical solutions and modern materials used in all phases of the process warrant a high level of safety, the possibility of different incidents is not fully excluded [3]. Such incidents endanger natural resources, primarily soil [4,5], water bodies and plants [6]. Depending on their

severity, they may for a certain period of time jeopardize the intended use of land on which the incident has occurred [7].

Heavy metals may be bound or absorbed by particular natural substances, which may increase or decrease mobility. Studying the dissipation of heavy metals is called speciation. Study shows that the speciation may be understood in different ways and in various aspects, but in all cases when we generally talk about different forms of existence of studied compounds we talk about speciation. Heavy metals (e.g. lead, copper, cadmium, zinc, chromium, etc.) are toxic even at low concentrations. As they are non-biodegradable, their threat is multiplied by their accumulation in the environment through the food chain. The detoxification of metal-bearing wastewater is a pressing environmental concern. The development and implementation of cost-effective process for removal/recovery of metals is essential in order to improve the competitiveness of industrial processing operations and to minimize the environmental hazard of toxic metal-containing effluents [8].

Biosorption

Biosorption is a physico-chemical and metabolically-independent process based on a variety of mechanisms including absorption, adsorption, ion exchange, surface complexation and precipitation. Biosorption processes are highly important in the environment and conventional biotreatment processes.. As a

branch of biotechnology, biosorption has been aimed at the removal or recovery of organic and inorganic substances from solution by biological material which can include living or dead microorganisms and their components, seaweeds, plant materials, industrial and agricultural wastes and natural residues. It is a metabolically passive process, meaning it does not require energy, and the amount of contaminants a sorbent can remove is dependent on kinetic equilibrium and the composition of the sorbents cellular surface. [9]. Contaminants are adsorbed onto the cellular structure.

The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases.

Tithonia Diversifolia

Tithonia diversifolia, commonly known as the wild sunflower, is a succulent and soft shrub that grows to a height of 1 – 3 metres; and bears alternately positioned leaves along most of the stem. Each leaf has 3 – 5 lobes with toothed margins, a pointed apex and a long petioles [10].

The leaf veins are parallel. The flower disc of *T. diversifolia* is about 3 cm in diameter and has yellow petals, 4 – 6 cm long. The plant flowers and produces seeds throughout the year. Each mature stem may bear several flowers at the top of the branches. The lightweight seeds can easily be dispersed by wind, water and animals [10]. *Tithonia diversifolia* originated from Mexico, and it is now widely distributed throughout the humid and sub-humid tropics in Central and South America, Asia and Africa [11]. *Tithonia diversifolia* was probably introduced into Africa as an ornamental plant. It has been reported in Kenya [12], Nigeria [13], Rwanda [14].

The research is aimed at revealing the efficiency of carbonized *Tithonia diversifolia* for the removal of cadmium from aqueous solution.

MATERIALS AND METHOD

Preparation of Adsorbent (Carbonized *Tithonia Diversifolia*): The *Tithonia diversifolia* used for this research were acquired from road side along the Ibokun-Ilesha Express Road in Ibokun, Osun State, Nigeria. The stems were washed thoroughly with water to remove debris, cut into smaller pieces and dried. The dried samples were then ground with a Victoria grain mill and sieved using 850 μm mesh screen. The sample obtained was carbonized at 300 °C for 2h using carbolite CWF 1100. The carbonized samples were then allowed to cool and fine particles obtained using 100 μm mesh screen sieve.

Preparation of Stock Solutions

Exactly 1.63g of cadmium chloride was weighed and dissolved in 1000 cm^3 volumetric flask and made up to the mark with distilled water.

pH Profile Studies

From the stock solution earlier prepared, 100 ppm of cadmium solution was prepared by measuring 100ml of the stock solution and diluted in 1000 cm^3 capacity volumetric flask and was made up to the mark using distilled water. 100 cm^3 of the metal solution was measured into 18 beakers and the pH adjusted from 1 to 6 in duplicate. Then 0.5g of the adsorbent was weighed and introduced into each of the labeled beakers. The experiment was allowed to stand for 6h with constant stirring, after the expiration of the 360 min, the solutions were filtered and 10 cm^3 of each was taken for metal analyses using Atomic Absorption Spectroscopy (AAS). The same procedure was used for copper metal solution.

Concentration Studies: Cadmium metal concentrations at; 25 ppm, 50 ppm, 75 ppm, 100 ppm, 150 ppm and 200 ppm of metal solutions were prepared and the pH was adjusted to 5. Then 100 cm^3 was measured into 12 different beakers for duplicate study with different concentration mentioned above. Exactly 0.5g of the adsorbent was weighed into each of the beakers. The solutions were allowed to stay for 2h in water bath for four different rounds of temperature which are; room temperature, 35°C, 45°C and

55°C. At the expiration of 2 hours, the solutions were filtered and 10ml of each of them was measured and taken for metal analysis. For copper analyses, the same experimental procedures were used except that the pH was adjusted to 4 and allowed for 3 hours.

Adsorption Capacity: For cadmium metal; 100 ppm metal solution was prepared, 100cm³ of it was measured and transferred into a beaker. The pH was adjusted to 5 and the mixture of metal solution and 0.5g of biomass was allowed to stay for 120 min. At the expiration of the optimum time, the solution was filtered and 10cm³ was measured out for analysis which was first cycle, the residue was scraped into another beaker and another 100cm³ l of the metal solution with optimum pH was measured and transferred into it, this was allowed for thirty minutes coupled with agitation. The procedure was repeated until 10 cycles were made and the same procedures were observed for copper metal but with optimum pH of 4 and allowed to stand for 180 min. The same process was repeated for copper

RESULT AND DISCUSSIONS

Effect of pH on the Adsorption Of Cadmium And Copper

pH Studies: pH study for the adsorption of metals using *Tithonia diversifolia* is useful in determining the optimum sorption of metal ions. It has been reported that adsorption increases as the pH of the solution increases [15].

Figure 1 is the plot of pH profile study for cadmium and copper ions. From Fig. 4.1, the uptake of copper (II) increases as the pH of the solution increases; at pH 1, pH 2, pH 3, pH 4 and pH 5, percentage metal bound were 20.59, 48.47, 94.26 and 94.08% respectively, at pH 5 and pH 6, percentage metal bound dropped to 93.26, 92.62% respectively. The percentage removal for copper is low at pH 1, it increased up to pH 4, remains high and almost constant in the pH range 7 - 8 in a study involving removal of some heavy metals by electrocoagulation [16]. The increase in the removal of copper as pH increases is due to the decrease in competition between proton and Cu²⁺ ion for the surface site. At low pH, the hydrogen ion competes with the metal cations for the exchange sites in the system which partially releases the metal cations [17].

Cadmium study showed that the optimum binding pH is 5 [18] [19] made similar assertions. At pH 1, pH 2, pH 3, pH4, pH 5 and pH 6, percentage bound were 25.59, 59.12, 96.76, 96.14, 96.98 and 98.31% respectively. The percentage removal for cadmium (II) ion is low at pH 1, it increased up to pH 5, and remained high and almost constant at pH 6. This is in line with other research work of Konstantinos *et al.*[16].

Adsorption Capacity

Presented in Figure 3 are plots of metal ions bound to the biomass with increase in the number of adsorption cycles. The plots show a downward trend as number of cycles increases.

Figure 2 is the plot of metal adsorbed for 10 cycles. As can be seen in this plot, percentage sorption capacity for Cd (II) ions at cycle 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 were 89.55, 87.43, 74.97, 67.47, 66.99, 64.15, 59.45, 55.70, 54.50 and 54.50% respectively. Reason for this high binding power at the initial stage is attributed to the biomass having maximum binding sites available for interaction. In the case of Copper, as shown in Figure 4; percentage adsorbed for Copper ion in the 1st, 2nd, 3rd, 4th, 5th, 6th, 7th, 8th, 9th and 10th cycle were 98.49, 95.05, 93.22, 85.74, 86.23, 84.74, 83.61, 82.68, 82.07 and 80.73% respectively. It has been suggested that sorption processes such as chemisorption, followed by fast ion exchange and physicosorption could be responsible for the metal binding [20]. From this result, there is no doubt that the biomass could still be potent beyond 10 cycles.

Initial Concentration Studies

Initial Concentration Studies for Cadmium:

Presented in Figure 3 are plots of percentage cadmium ions bound to the biomass as a function of changes in concentration and variations in temperature. The plots show a gradual decrease in percentage metal bound as temperature increases.

Initial Concentration Studies for Copper (II)

Ion: Presented in Figure 4 are plots of percentage copper ions bound to the biomass as a function of changes in concentration and variations in

temperature. The plots show a gradual decrease in percentage metal bound as temperature increases. The effect of initial cadmium concentration and initial copper concentration on adsorption (investigated under the specified conditions; initial pH of 5 for cadmium and 4 for copper; contact time of 120 min for cadmium and 180 min for copper; adsorbent dosage of 0.5g; and temperature of room, 35, 45, 55°C) were carried out.

Effect of Initial Concentration for Cadmium

Fig.4 shows that the removal of cadmium was dependent on the concentration of cadmium as the increase in the initial concentration decreased the amount of cadmium removed [21]. For cadmium with the initial concentration of 25ppm, the percentage cadmium removal at room temperature, 35, 45, 55°C were 99.62, 98.98, 97.52 and 96.90% respectively; percentage removal for the initial concentration of 50ppm at room temperature, 35, 45 and 55°C were 98.963, 98.74, 96.66, 96.49% respectively; for the initial concentration of 75ppm, the percentage bound values at room temperature, 35, 45, 55 and 65°C were 98.58, 98.07, 95.93, and 94.45% respectively. From Figure 4.7, it can be deduced that increase in the initial concentration of metals leads to decrease in the percentage metal bound.

Effect of Initial Concentration for Copper

In the case of copper as can be seen in fig.4, The percentage Copper removal using initial concentration of 25 ppm at room temperature, 35, 45 and 55°C were 98.58, 96.51, 94.80 and 93.17%; the percentage removal using initial

concentration of 50 ppm at room temperature, 35, 45 and 55°C were 98.04, 96.92, 92.92 and 90.43%; percentage removal using initial concentration of 75 ppm at room temp., 35, 45 and 55°C were 97.57, 95.03, 91.27 and 87.82% respectively; It can be seen that the removal of copper was dependent on the initial concentration

of copper, as decrease in the initial concentration increased the amount of metal removed [21]. The decrease in percentage sorption as concentration increases may be a result of a reduction in the number of available functional groups on the adsorbents as the initial concentration is increased.

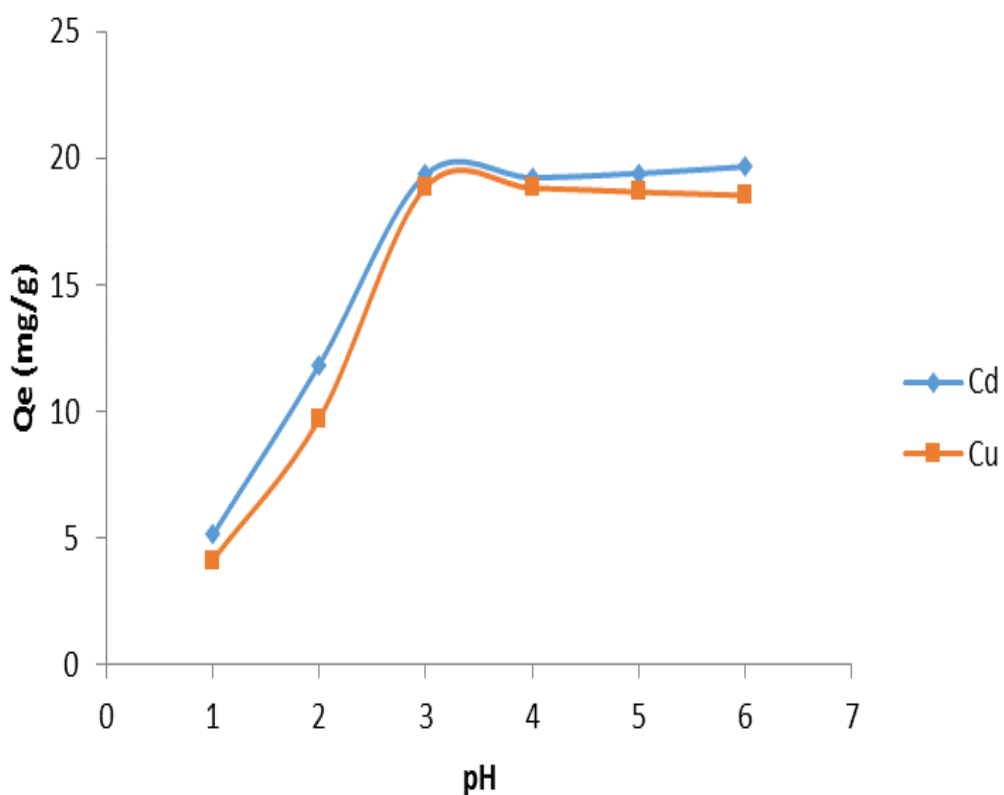


Figure 1: Effect of pH studies

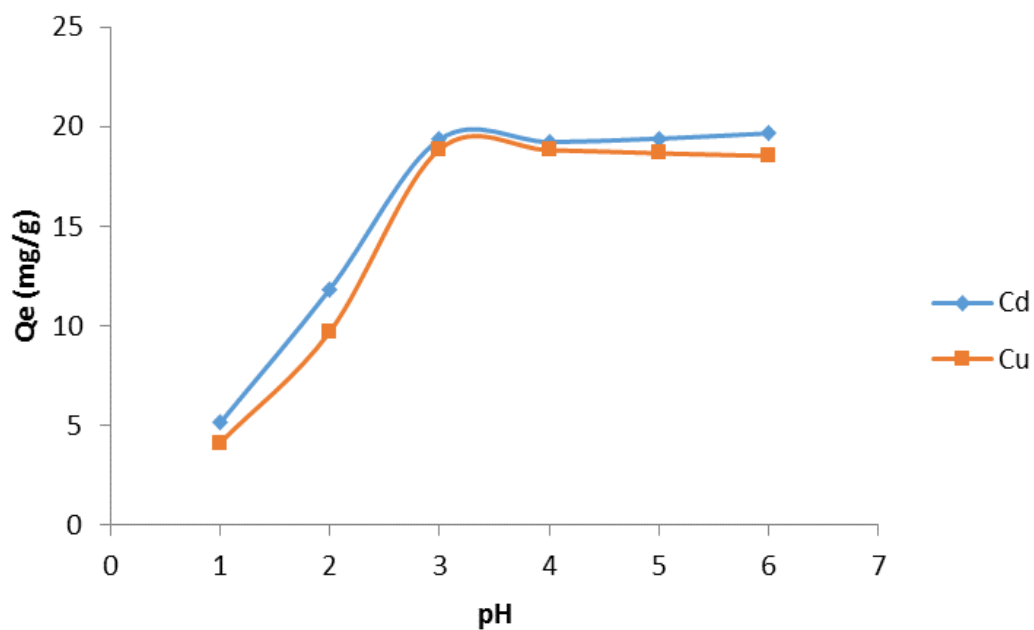


Figure 2: Plot of Adsorption Capacity

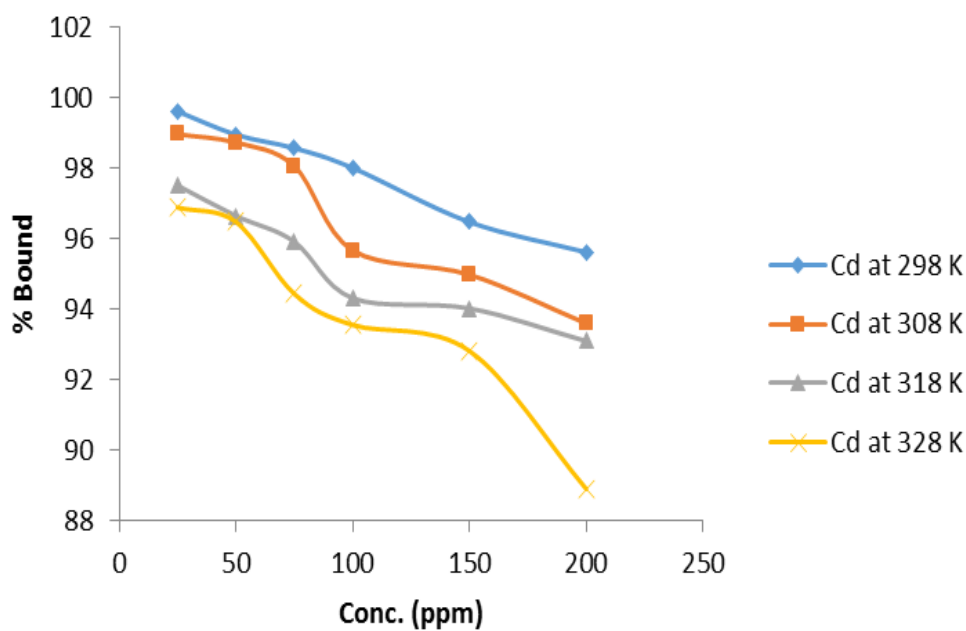


Figure 3: Plot of Effects of Initial Concentration for Cadmium (II) Ion

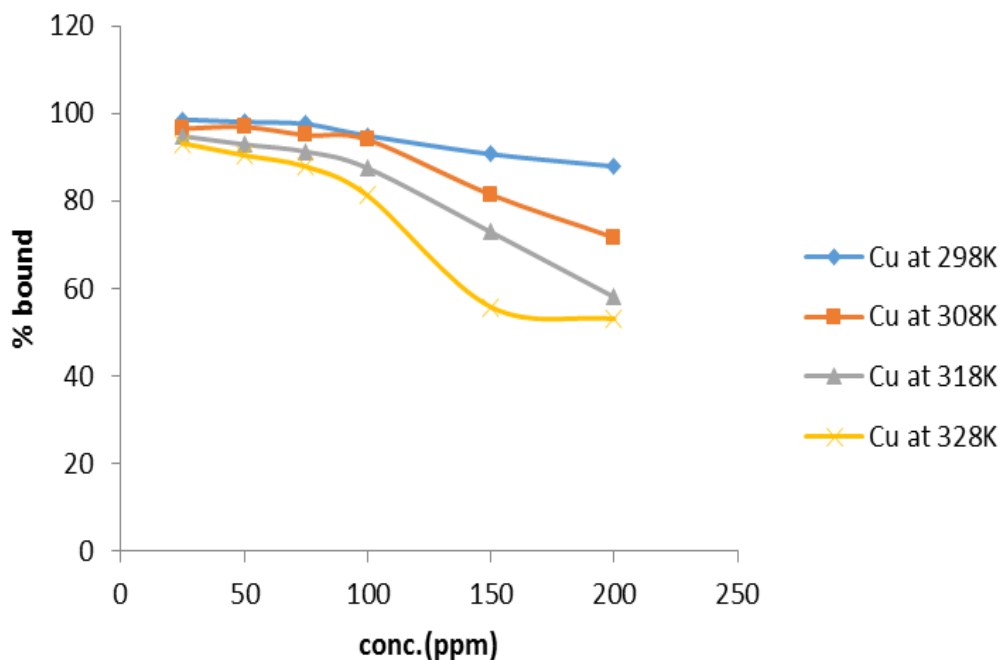


Figure 4: Plot of Effects of Initial Concentration for Copper (II) Ion

CONCLUSION

From the adsorption studies carried out, under different conditions such as pH, concentration, and adsorption capacity, the amount of Cu^{+2} and Cd^{2+} adsorbed was found to vary with the initial solution pH, adsorbent dosage, and concentration. Therefore, carbonized *Tithonia diversifolia* is found to be an excellent adsorbent for the removal of diverse heavy metals.

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