

Dried Orange Peel: A potential Bio sorbent for Removal of Cu (II) and Cd (II) Ions from Aqueous Solution

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Abstract:

Bio sorption is one of potential alternative conventional technologies for the removal of metal ions from aqueous solutions due to its low cost, high efficiency, minimization of chemical or biological sludge, regeneration of bio sorbents and possibility of metal recovery. Therefore the aim of this study was to study effect of operational parameters on dried orange peel: a potential bio sorbent for removal of Cd (II) and Cu (II) ions from aqueous solution. Batch adsorption experiments were performed as a function of pH, contact time, solute concentration and adsorbent dose and the residual metal ion concentrations were determined using flame Atomic Absorption Spectrometer (FAAS). The results indicate that optimum conditions for copper (II) and cadmium (II) adsorption were achieved with contact time of 120 minutes and dose of orange peel 2 g at pH 2 and 6 respectively. The orange peel yielded a maximum adsorption efficiency of 99.23% for copper (II) ion and 97.75% for cadmium (II). The fitness of the bio sorption data for Langmuir and Freundlich adsorption models was investigated and the calculated equilibrium data fitted well to both Langmuir with correlation coefficient (R^2) of 0.988 for Copper (II) and 0.979 for cadmium (II) ion and Freundlich with correlation coefficient (R^2) of 0.995 for copper (II) ion and 0.998 for cadmium (II) ion. The maximum adsorption capacity (q_{max}) of orange peel was found to be 4.15 mg/g for copper (II) ion and 2.45 mg/g for cadmium (II) ion.

Keywords: Cu⁺², Cd⁺², adsorption capacity, adsorption isotherm, bio sorption, Orange peel

1. Introduction

The removal and recovery of toxic heavy metal ions from wastewater is of great importance from an environmental view point. Heavy metals, such as Cu, Zn, Pb and Cd, are prior toxic pollutants existent in industrial wastewater, while they also constitute common groundwater contaminants (Stylianou, Hadjiconstantinou, Inglezakis, Moustakas, & Loizidou, 2007). Among those, Copper is an essential element, acute does cause metabolic disorders. Inhalation of copper produces dermatitis. Chronic copper poisoning among other causes hemolytic anemia, neurological abnormalities and corneal opacity (Mohan, Pittman Jr, & Steele, 2006). Due to the toxic effect the permissible limit of copper effluent discharge is limited to 0.25 mg/l, as per the Environmental protection Agency (EPA) USA. However some countries even have lower permissible limit such 0.05-0.1mg/l in Hong Kong and Japan and 0.20mg/l in Malaysia (Zhu, Fan, & Zhang, 2008). Copper is a toxic heavy metal discharged in to the environment due to industrial operations carried out by brass industries, electrical goods production, electro deposition of metals, metallurgical processes, copper-ammonium rayon industries, mining and battery manufacturing (Mallick, 2002), and agricultural activities (Hawari & Mulligan, 2006). Copper containing waste waters are waste products of various chemical industries, such as mining, smelting, extracting, and finishing processes. It is a highly toxic element and an excessive in take results in its accumulation in the liver and production of gastrointestinal problems, therefore its removal from wastewater is high importance (Alkan & Doğan, 2001). Copper present in industrial waste is primarily in the form of bivalent Cu (II) as a hydrolysis product or CuCO₃ or in the form of organic complexes. In copper cleaning, copper plating and metal processing industries Cu (II) concentrations may approach 0.1-0.12g/l, which has to be reduced to 0.0010-0.0015g/l according to water quality standards to render the waste water to be free from the toxicity (Ekmekyapar, Aslan, Bayhan, & Cakici, 2006). Beyond the threshold concentration of >0.002 g/l they become toxic to plants and animals (Kiran, Kaushik, & Kaushik, 2007). Cadmium is also one of the heavy metals, which is highly toxic to human, plants and animals. The metal is of special concern because it is non-degradable and therefore persistent. The main anthropogenic pathway through which cadmium enters environment is via wastes from industrial processes such as electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium nick batteries, fertilizers, pesticides, mining, pigments and dyes,



textile operations and refining (Salim, Al-Subu, & Sahrhage, 1992). Cadmium is a toxin of environmental concern. The impact for non-cancer causes includes kidney, liver, and lung damage (Volesky, 2003). It is also classified as a probable human carcinogen for lung cancer. The association of cadmium with hormone-related cancers such as prostate and breast cancers has been actively investigated since the initial implication (Åkesson, Julin, & Wolk, 2008). There is no known function of cadmium in the human biological system. The presence of such foreign metal ion in the human is likely a result of various exposures. In addition to direct exposure from air and drinking water, another potential exposure is to result from crops grown in the contaminated water and soil environment, which transports the metal into food chain where cadmium is accumulated in various parts of crops (Lebeau, Bagot, Jézéquel, & Fabre, 2002).

Many toxic heavy metals have been discharged into the environment as industrial wastes; causing serious soil and water pollution. They are also common groundwater contaminants at industrial and military installations. The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently. It is well known that the consumption of copper contained water causes various health problems to living organism and transmits to the food, especially shellfish, liver, mushrooms and nuts (Antunes, Luna, Henriques, & da Costa, 2003). Intake of over dosed copper by humans may cause to severe mucosal irritation, hepatic and renal damage, widespread capillary damage, gastrointestinal irritation and central nervous problems (Larous, Meniai, & Lehocine, 2005). The release of heavy metals into our environment is still large. In certain areas of the world it is even increasing. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. It is well known that some metals can have poisonous or otherwise toxic to human beings and ecological environments, include chromium, antimony, copper, lead, mercury, cadmium, manganese etc (Jak, Maas, & Scholten, 1996). Even though these exist several methods for removing heavy metals such as chemical precipitation, membrane filtration, ion exchange liquid extraction electro analysis etc. Most of these methods can't be used due to their high cost and low feasibility for small scale industries (Mansour, Al-Hindi, Yahfoufi, Ayoub, & Ahmad, 2018). In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost. Conventional adsorbents such as granular or powdered activated carbon are not always popular as they are not economically viable and technically efficient (Åkesson et al., 2008). Therefore numerous approaches have been studied for the development of cheap and effective metal sorbents, such as fly ash (Ricou-Hoeffler, Lecuyer, & Le Cloirec, 2001), peat (Yuh-Shan Ho & McKay, 2000), microbial biomass (Ahluwalia & Goyal, 2007), and agricultural byproducts (Jaramillo, Gómez-Serrano, & Alvarez, 2009). Another cheap and unconventional adsorbent particularly suited to adsorption is fruit residue, such as apple, banana, and orange peel (Feng, Guo, & Liang, 2009). The use of orange peel as an adsorbent material presents strong potential due to its high content of cellulose, pectin (galacturonic acid), hemicellulose and lignin. These components bear various polar functional groups including carboxylic and phenolic acid groups to be involved in metal binding (Matheickal, Yu, & Woodburn, 1999) and are biopolymers admittedly associated to the removal of heavy metals (Gaballah, Goy, Kilbertus, & Thauront, 1994). As a low-cost adsorbent, orange peel is an attractive option for the adsorption removal of dissolved metals. Orange peel is abundant in soft drink industries and usually treated as wastes. It is mostly composed of cellulose, pectin, hemi-cellulose, lignin, chlorophyll pigments and other low relative-molecular-mass hydrocarbons (Feng et al., 2009). These components contain many hydroxyl functional groups (OH), which makes it a potential matrix to synthesize orange peel. Recent studies have demonstrated the utilization of orange residues for the study of metal adsorption due to the great renewable production and low cost for these adsorbents (Kurniawan, Chan, Lo, & Babel, 2006). Moreover the waste from the orange juice industry has been regarded as a potential biosorbent material for removing Cd^{2+} from aqueous solutions (Pérez-Marín et al., 2007).

Even though various modification techniques are reported in the literature to overcome the above problems there is no sufficient works reported on the dried orange peel: a potential biosorbent for removal of Cd (II) and Cu (II) ions from aqueous solution. Therefore, the impetus behind this study was to study effect of operational parameters on dried orange peel: a potential biosorbent for removal of Cd (II) and Cu (II) ions from aqueous solution.

2. Materials and Methods

2.1. Apparatus and Instruments

The apparatus and instruments used in this project include: pH meter (MP 220) to measure pH of the solution, FAAS spectrophotometer (BUCK 210VGP) to measure metal concentration, Rotary shaker (SO1 Orbital shaker, UK) to agitate the sample, Balance (OHAUS, Switzerland) for weighing, Discator (SD-504 Nikko Japan super dry) to keep a sample less humid, Electrical mill (IKA WERKE) to grind sample, Sieve number 1mm to get 1mm particle size, Hot Air Oven (260 M contherm) to dry sample and Filter paper Whatman No_1 to filter the solution.

2.2. Chemicals and reagent

Analytical grade reagents: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ were used for preparing the corresponding metal ion pollutions. HCl and NaOH were used to adjust pH values of solutions. Ethanol and distilled water were used in the experiment as solvent.

2.3 .Experimental Methods and Procedures for Biosorption Study

2.3.1. Experimental site

This study was carried out by collecting waste orange peel from Harar city which is located in the Eastern part of Ethiopia. The batch mode adsorption experiment was done at Haramaya University, Chemistry Research Laboratory.

2.3.2. Preparation of bio sorbent (adsorbent)

The orange peel was collected from local sources and was washed with double distilled water to remove external dirt. Wet orange peels were kept in air for removing the free water from the surface and dry in oven for 24 hours at 70°C. The dried orange peels were ground into powder and kept in an air tight bottle prior to the experiments. 50 g of dried orange peel powder was sieved and soaked in 250 mL ethanol and then treated with 250 mL 1% NaOH solution at room temperature for 24h to remove chlorophyll pigments and other low relative molecular mass compounds. The resulting mixture after, decantation and filtration was washed with double distilled water until the solution reached a neutral pH value around 7.0 and was dried at 70°C in an oven 6-8 hrs.

2.3.3. Preparation of adsorbate solutions (synthetic solution)

Copper (Cu (II)) solutions: Solutions of Cu (II) ions were prepared by dissolving calculated amount of copper in distilled water, so as to achieve concentrations of 1000mg/L in the flask. Different concentrations of metal ions were prepared by diluting this stock solution. The pH of the solution was adjusted using 0.1N HCl and 0.1N NaOH to achieve the desired values. Cadmium (Cd (II)) solutions: 1000 mg/L concentration was prepared by dissolving calculated amount of cadmium sulfate in distilled water. The stock solution was further diluted to obtain solutions of various known concentrations of cadmium (II) ions. The pH of the solution was adjusted using 0.1N HCl and 0.1N NaOH to achieve the desired values.

2.4. Adsorption Isotherm

Adsorption isotherm is a curve which relates the amounts of adsorb ate adsorbed per unit mass of adsorbent to the amount of unadsorbed adsorb ate remaining in solution at equilibrium time. Several models have been developed to describe adsorption system behaviors. But the most common models are the Langmuir and Freundlich models. Both the Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1907) sorption models were used to fit metal sorption by Orange peel to evaluate the mechanistic parameters associated with the sorption process. Adsorption on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the certain conditions. The Langmuir isotherm: the Langmuir isotherm assumes uniform energy of sorption on to the surface and no transmigration of sorbate on the surface (Benjamin & Leckie, 1981). The Langmuir isotherm is given by the formula below

$$Q = \frac{Q_{max}C_{eq}}{1 + bC_{eq}} \text{-----} 1$$

Where, q is milligrams of metal accumulated per gram of the biosorbent material;

C_{eq} is the metal residual concentration in solution;

Q_{max} is the maximum specific uptake corresponding to the site saturation and

B is the ratio of adsorption and desorption rates.

The linearised isotherm allows the calculation of adsorption capacities and Langmuir constants and is equated by the equation

$$\frac{C_{eq}}{q} = \frac{1}{bQ_{max}} + \frac{C_{eq}}{Q_{max}} = \frac{1}{Q_{max}} \left(\frac{1}{Cb} + \frac{C_{eq}}{Q_{max}} \right) \quad \text{----- 2}$$

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter RL , which is defined by

$$RL = \frac{1}{1+bC_0} = \frac{1}{c \left(\frac{1}{C_0} + b \right)} = \frac{1}{1+mg/l} \quad \text{----- 3}$$

Where C_0 is the initial adsorbate concentration (mg/l) and b is the Langmuir constant. RL indicates the isotherm shape and whether the adsorption is favorable or not.

Table 1: Type of isotherm for various RL

RL	Type of isotherm
$RL > 1$	unfavorable
$RL = 1$	linear
$0 < RL < 1$	Favorable
$RL = 0$	irreversible

The Langmuir model assumes that the uptake of metal of ions on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. However, the Freundlich model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption (Bulut & Baysal, 2006). The Freundlich isotherm is empirical and describes multi layered adsorption of metal ions on sorbent surface. The Freundlich model provides a more realistic description of metal adsorption by organic matter because it accounts for sorption to heterogeneous surface or surfaces supporting sites of varied affinity. In contrast to Langmuir model. The Freundlich model does not assume saturation of metal sorption. The Freundlich model assumes that stronger decreases with increasing degree of site occupation by metal ions. For fitting the model to experimental data, the Freundlich model generally gives a better fit for higher equilibrium concentration of metal in solution.

$$Q = K_f C_{eq}^{1/n} \quad \text{----- 4}$$

Where, C_{eq} is the equilibrium concentration (mg/l)

Q is the amount adsorbed (mg/l)

K_f and n are constant.

2.4.1. Batch Mode Adsorption Studies

Batch mode adsorption studies for individual metal ions were carried out in 250mL Erlenmeyer flask to investigate the effect of different parameters such as adsorbent concentration, adsorbent dosage and pH of the solution on the removal efficiency of each metal ion. Standard metal ions of the selected ion were mixed with appropriate orange peel grind and agitate at 180rpm. The resulting solution of each of metal ions were filtered. Filter paper and the filtrate were analyzed for the corresponding metal ion concentration. Finally the filter solution was determined by its absorbance using atomic absorption spectrophotometer.

2.4.1.1. Effects of various parameters on the Metal ions Adsorption Effect of the Bio sorbent

Batch mode adsorption studies for individual metal ions were carry out in 250mL Erlenmeyer flask to investigate the effect of different parameters on the removal efficiency of each metal ion standard metal ions of the selected ion was mixed with appropriate orange peel grind and agitate at 180rpm .The resulting solution of each of metal ions were filtered with a filter paper and the analyzed for the corresponding metal ion concentration. Finally, the filtered solution was determined by its absorbance using atomic absorption spectrophotometer. A standard solution of metal ions (known concentration) was taken as a 250ml Erlenmeyer flask each time for each of metal ions under investigation and mixed with a certain fixed dosage of the powdered orange peel. The contents in the flask were agitated by a shaker at 180 rpm by varying the contact time in each experiment. After filtration the filtrate in each case was analyzed for the resulting metal ion concentration using Flame Atomic Absorption Spectrophotometer removal efficiency was finally calculated by using the relationship

$$\text{Adsorption (\%)} = \frac{[(C_o - C_e)/C_o] \times 100}{\text{-----}} \quad 5$$

Where, C_o = the initial concentration (mg/L) and

C_e = final concentration (mg/L) of the metal ions being studied .the adsorption capacity

(q_e) of the orange peel will calculate as:

$$q_e = \frac{(C_o - C_f) \times V}{M} \text{-----} \quad 6$$

Where q_e = adsorption capacity of biomass (mg/g)

V = the volume of reaction mixtu

M = the mass of adsorbent use (g)

C_o = the initial concentration (mg/L)

C_f = final concentration (mg/L) of the metal ions

2.4.1.2. Effect of pH

The pH of the solution was one of the important factors governing the adsorption of heavy metals ions. Initial pH was have a critical role in metal adsorption by influencing the function groups on the adsorbent surface and also the metal's solubility .The pH range of solutions were adjusted to 4 – 8 for Cd(II) and Cu(II) ions to determine the effect of solution acidity on the efficiency of adsorption by keeping the other parameters constant .

2.4.1.3. Effect of metal ion concentration

This step was determined the effect of metal ion concentration on metal removal efficiency of adsorbent (orange peel). Different metal ions concentrations (10, 20,30,40,50 and 60 mg/L) was prepared to investigate the effect of metal ions concentration. Other parameters were kept constant .All concentrations were obtained from a stock solution of 1000mg/L of each metalionwhile each the other parameters were kept constant.

2.4.1.4. Effect of adsorbent dosage

To determine the effect of adsorbent dosage on the metal ions removal efficiency of powdered orange peel, different weights of the biomass, ranging from 0.5g - 5g were dispersed in 250ml flask with metal ions concentration of 50gml/L and by keeping the other parameters constant. The solution was adjusted to the optimum pH in which maximum bio sorption of the metal ion occurred.

2.4.1.5. Effect of contact time

Constant time was also important parameters for the assessment of practical application of sorption process. For studying the rate of metal ions biosrption by the orange peel powder the quantity of metal ion adsorbed was determined by varying the constant time from 30 up to 180min with a difference of 30 min between measurements; the other parameters were kept constant in all cases.

2.5. Data Analysis and Inter Pretentions

The concentrations of the selected metal ion were determined in all measurements using (AAS). After conscious processing the sample through various methods the data generated was analyzed by (SAS) to compute the mean, standard deviation and by linear regression values. The adsorption capacity of an orange peel was evaluate by adsorption isotherms described by Langmuir and Freundlich isotherm models. The final results were then presented respectively in tables and plots.

3. Result and Discussion

3.1. The Optimum Conditions for Cu (II) and Cd (II) ions Removal by Orange peel

3.1.1. Effect of adsorbent dosage

The effect of the adsorbent dose was studied at room temperature by varying the adsorbent amounts from 0.5 to 5 g/100 mL. For all these runs, initial concentration of Cu (II) and Cd (II) ions, pH, and agitation speed and contact time was kept constant. Figure 1 shows the adsorption efficiency of different doses of the bio sorbent. The uptake of both Cu (II) and Cd (II) ions was found to increase rapidly with increasing concentration of bio sorbent up to a bio sorbent dose of 3 g. The increase in the adsorption efficiency can be attributed to the increased number of available sites for exchangeable ions to get adsorbed on its surface. Beyond this dosage level, however, the increase in adsorption efficiency of the material for both metal ions is observed to be marginal and this may be attributed to possible reduction of the adsorbent to the adsorbate ratio.

Therefore, the optimum adsorption efficiency of orange peel powder removal of both Cu (II) and Cd (II) ions can be achieved with adsorbent dose of 3 g/100 mL. In all subsequent studies, this amount of the adsorbent (3/100ml) was considered.

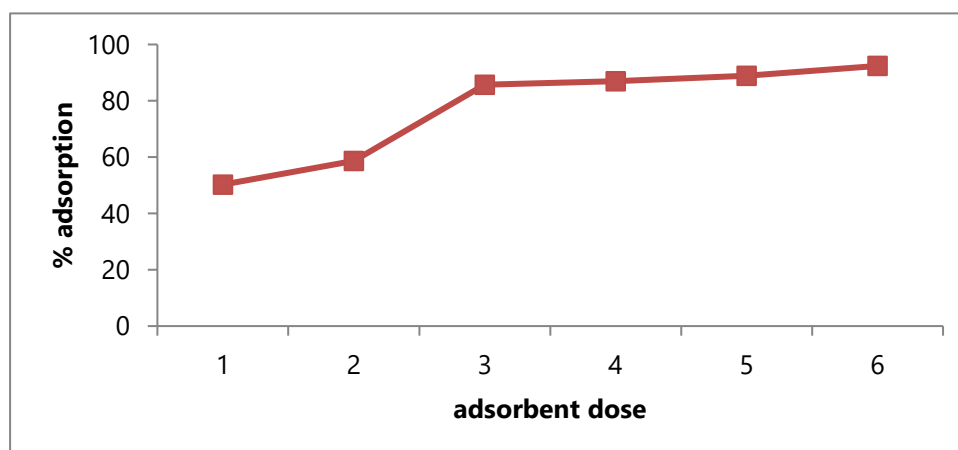


Figure 1. Effect of absorption dose on Cu (II) ions removal efficiency ($C_0=40\text{mg/L}$, $\text{pH}=4$, $\text{time}=120\text{ min}$, $\text{agitation speed}=180\text{ rpm}$)

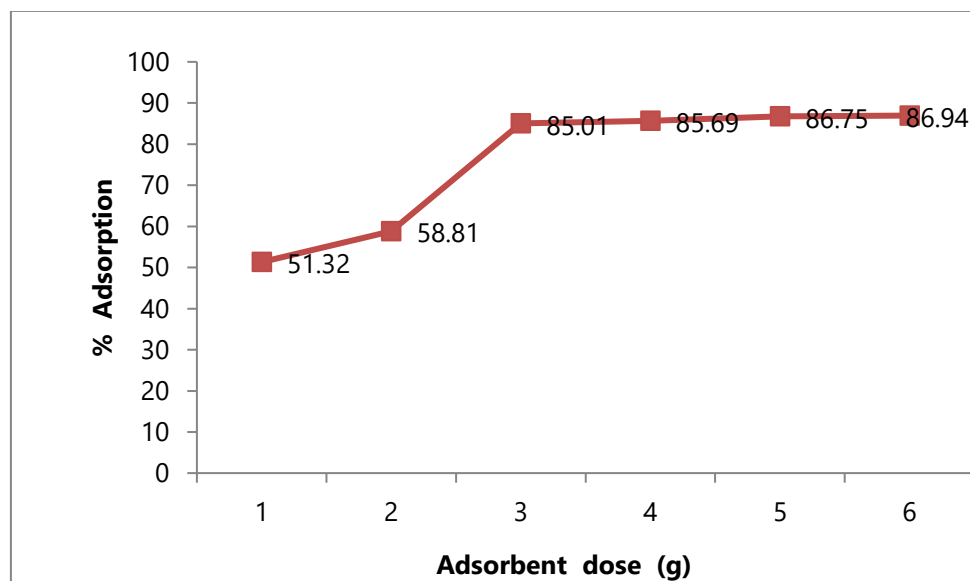


Figure 2. Effect of adsorbent dose on Cd (II) ions removal efficiency (Co =50mg/L, pH = 6, time = 150 min, agitation speed 180 rpm).

The sorption efficiency increased with an increase in adsorbent dosage and it goes on with little variation on further increment of the adsorbent dose. This trend was found to be similar for both of the metal ions at the higher concentration. This is due to an increase in the surface area of the bio sorbent which in turn increases the number of binding sites (Esposito, Pagnanelli, Lodi, Solisio, & Veglio, 2001). However, at high sorbent dosages, the available metal ions are insufficient to cover all the exchangeable sites on bio sorbent surface, resulting in low metal uptake. The plots in Fig 1 and 2 show that increase in adsorbent loading increases the percentage removal of Cu (II) and Cd (II) ions continuously until mass of the bio sorbent reached almost 3g. The removal efficiency increases from 50.2% to 86.5% and 51.32% to 86.94% for Cu (II) and Cd (II) ions respectively as the adsorbent dose increases from 0.5g to 5g. This increase in percentage adsorption could be the result of the number of available sites which apparently increased with the mass of the adsorbent. However, further increase in adsorbent dosage did not bring out significant increase in adsorption. At this stage, almost all the metal ions might have been removed such that further increase in the adsorbent dosage will not bring about appreciable adsorption. Therefore, the maximum removal efficiency for both cadmium (II) and (II) ions was obtained at an adsorbent dosage of 3g.

3.1.2. Effect of contact time

The time-course studies on the bio sorption of copper and cadmium ions were performed by contacting 100 mL of 50 mgL⁻¹ metal solutions with 3g orange powder. Both metal ions showed a fast rate of sorption up to 120 min of the sorbate-sorbent contact (Fig 3 & 4), during which period the metal ions removal from the solution of copper and cadmium increased from 65.5±0.44 to 91.55±0.33 and 59.54 ±0.13 to 85.18±0.13 respectively. The second stage represented the slower progressive adsorption lasted for the next 120 min. The rapid stage may be probably due to the abundant availability of active sites on the biomass, and with the gradual occupation of these sites, the sorption process becomes slower (less efficient).

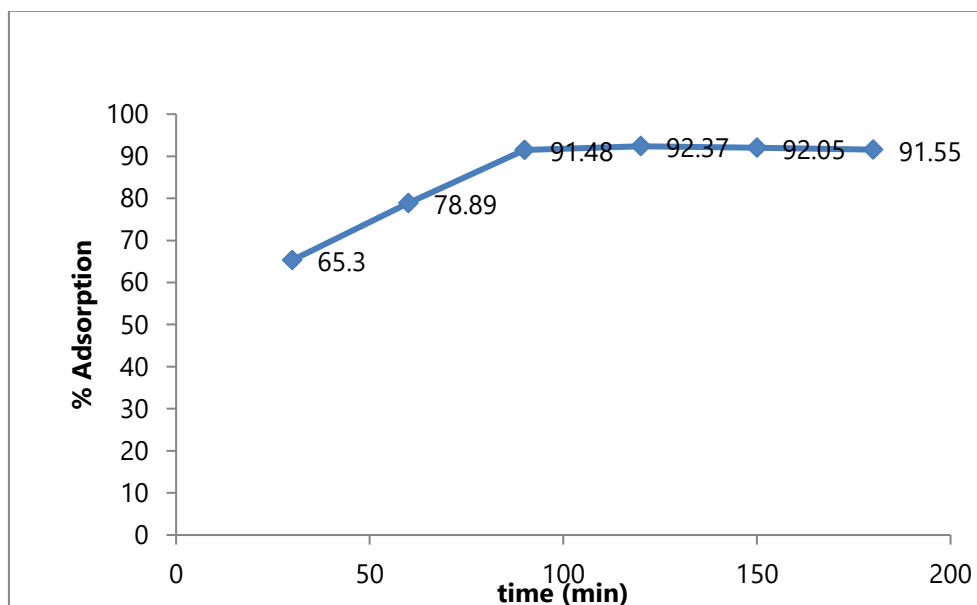


Figure 3. Effect of Copper (II) ions removal efficiency at various contact time ($C_0=40\text{mg/L}$, dose=2g, time = 120 min., agitation speed = 180rpm)

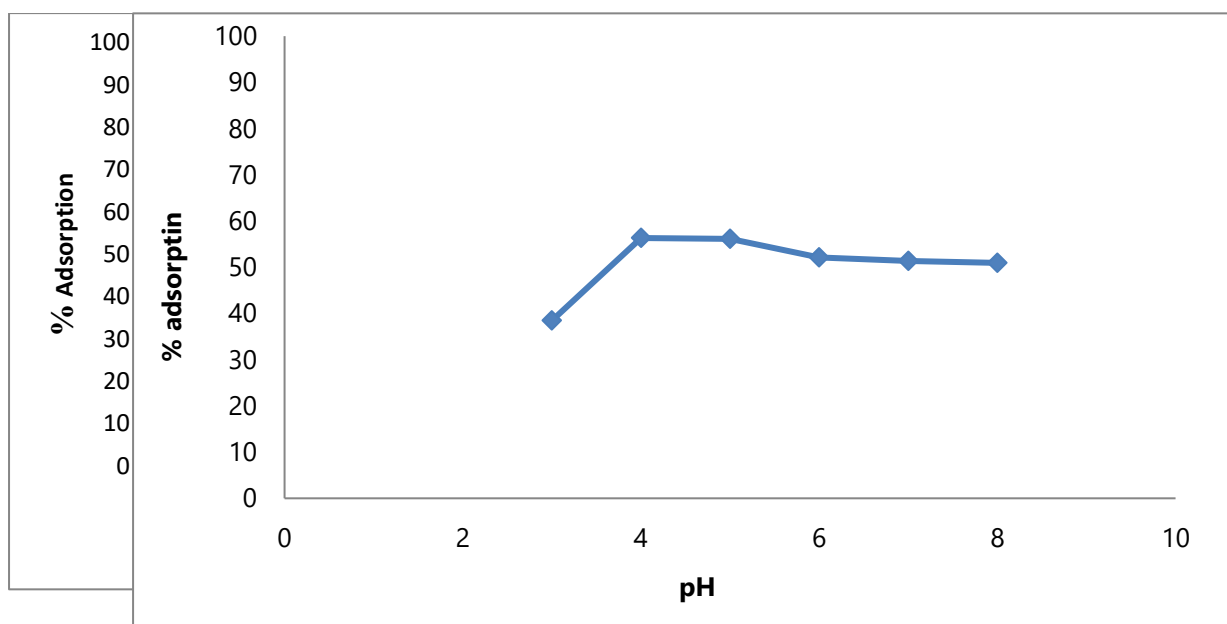


Figure 4. Effect of Cadmium (II) removal efficiency at various contact time $C_0=40\text{mg/L}$, dose=2g, time = 120 min., agitation speed = 180rpm)

At contact time 120 min the amount of the respective metal ions adsorbed on the sorbent were in a state of dynamic equilibrium with the amount of metal ions desorbed from sorbent and the increment became stable. Hence the optimum contact time for Cu (II) and Cd (II) ions were 120 minutes.

3.1.3. Effect of pH

The pH of the adsorbate solutions has been identified as the most important parameter governing sorption of metal ions on different adsorbents. This is partly due to the fact that hydrogen ions themselves are strong competing sorbates and partly that the solution pH influences the chemical speciation of metal ions. In order to establish the effect of pH on the biosorption of Cu (II) and Cd (II) ions, the batch equilibrium studies at different pH values were carried out in the range of 3 to 8 for the two metals (Fig 5 and 6).

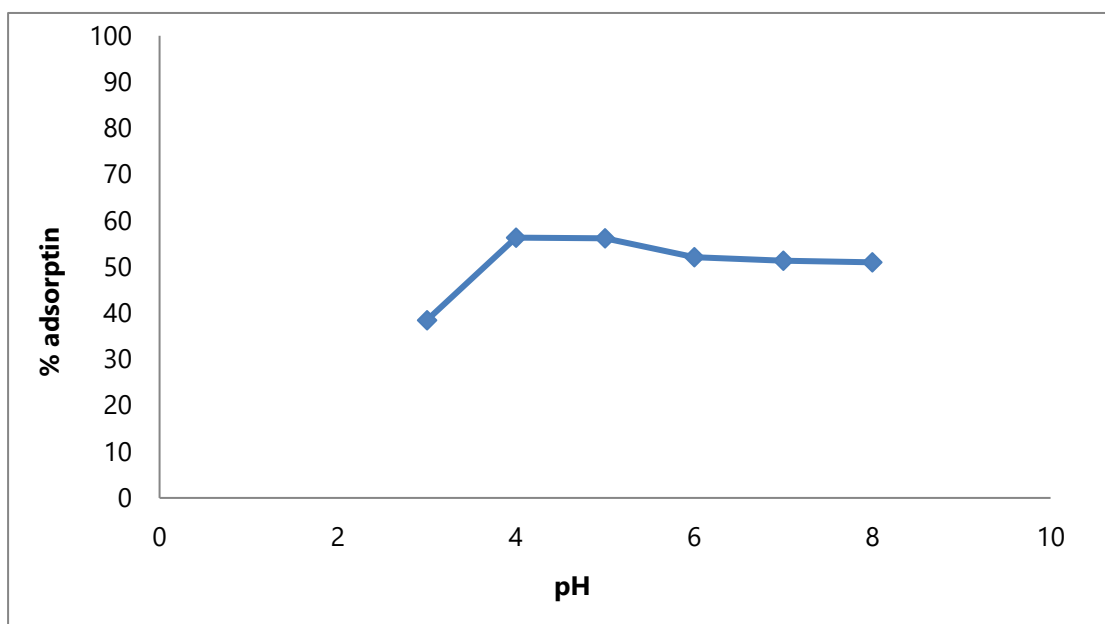


Figure 5: Effect of solution pH on Cu (II) ions removal efficiency ($C_0=40\text{mg/L}$, dose=2g, time = 120 min., agitation speed = 180rpm)

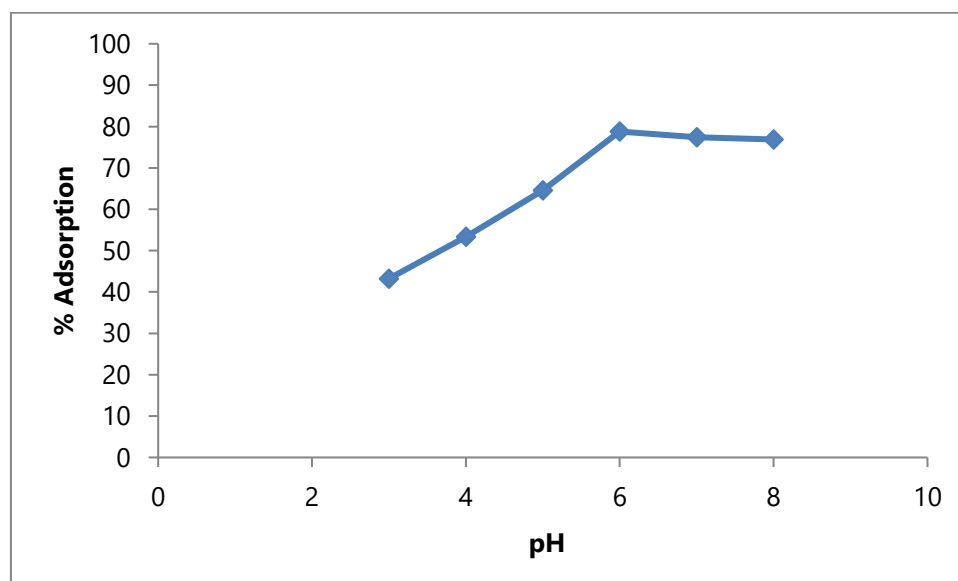


Figure 6. Effect of solution pH on Cd (II) ions removal efficiency ($C_0 = 50\text{mg/L}$, dose = 2g, time = 150 min., agitation speed 180 rpm).

The pH of metal solution played an important role in the bio sorption of heavy metal ions. In the present work, the extent of bio sorption was investigated in the range 3.0 to 8.0 with a constant amount of orange peel of 3g by adjusting the concentrations to 40 mg/L and 50mg/L for copper and cadmium respectively. The removal of the metal ions under consideration was affected by changes in pH. It was observed that removal of Cu (II) ion increased continuously in the pH range of 3 to 4 and then started decreasing in the pH range of 4 to 8. The removal efficiency of the adsorbent for Cu (II) ions increased from 38.45 ± 0.97 to 78.46 ± 0.68 as pH increased from 3 to 4. Maximum removal of Cu (II) ions by the adsorbent was found at pH 4. Further increase in pH above 5 led to decrease in the adsorption of copper (II) ions (fig5). Similarly figure 6 shows that Cd (II) ions removal efficiency increased in the pH range of 3 to 6. As it can be shown from the figure 6 the removal efficiency of the adsorbent for Cd (II) ions increased from 43.23 ± 0.17 to 76.85 ± 0.57 as pH increased from 3 to

6. The optimal Cd (II) ions removal by the absorbent was found to be at about pH 6. The influence of metal ion solution pH on the extent of adsorption onto the surface of the orange peel powder is shown in Fig. 6. Cd (II) ions up to pH 6, the increase in Cd (II) ion adsorption was gradual, but increased drastically for pH > 6. At higher pH (>6), the metal ion adsorption remain almost constant throughout the experiment. The removal efficiency the bio absorbent for Cd (II) ion ranged from 48.76 % to 95.24 % in the pH range of 1 to 6 and the maximum removal efficiency was attained at pH 6. This result was in agreement with those reported by (Srivastava, Mall, & Mishra, 2008). For the adsorption of Cd (II) ions onto orange peel and for the removal of the same per liter. The cause for decreasing of Cd (II) ions removal at very low pH value may be due to a significant electrostatic repulsion existing between the positively charged surface of the orange peel and the metal ions. As the pH of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases. A negatively charged surface site on the orange peel favors the adsorption of metal ions due to electrostatic attraction. Accordingly For pH values of 6 and beyond the Cd (II) ions adsorption onto the orange peel surface would first attain its maximum level and then remain nearly constant. This may also be partly attributed to chemisorptive adsorption of metal ions onto orange peel. This is supported by the fact that adsorption process of metal ions is not completely reversible and desorption from the spent orange peel powder would be on the lower side due to the chemisorptive nature of adsorption (Srivastava et al., 2008).

3.1.4. Effect of initial concentration of metal ions

Result of the study on the influence of initial metal ion concentration on the removal efficiency of the orange peel is depicted in Figures.7. From the figure it can be noted that the removal of the two metal ions by the orange peel surface has decreased from 96.91 ± 0.11 at 10 mgL^{-1} to 79.15 ± 0.20 at 60 mgL^{-1} Cu (II) and 98.12 ± 0.82 at 10 mgL^{-1} to 76.31 ± 0.07 at 60 mgL^{-1} Cd (II) ions. At low concentrations, the number of moles of metal ions in both cases is relatively small as compared with the number of adsorption sites on the adsorbent. In effect the adsorption process will have the maximum removal efficiency at the lowest value of initial metal ions concentration. However, as the metal ions concentration is getting higher and higher, most of the surface sites will be occupied by the adsorbed metal ions and availability of free sites is becoming fewer and fewer for further adsorption. In consequence, the percentage removal of metal ions which depends up on the metal concentration decreases (L. J. Yu, Shukla, Dorris, Shukla, & Margrave, 2003).

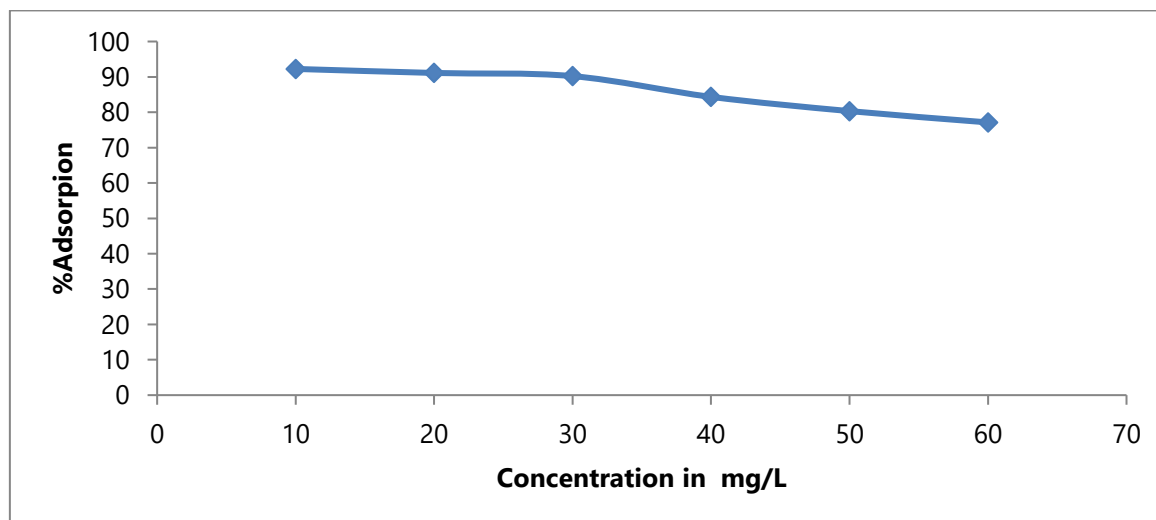


Figure 7: Effect of initial metal concentration on copper and copper removal efficiency

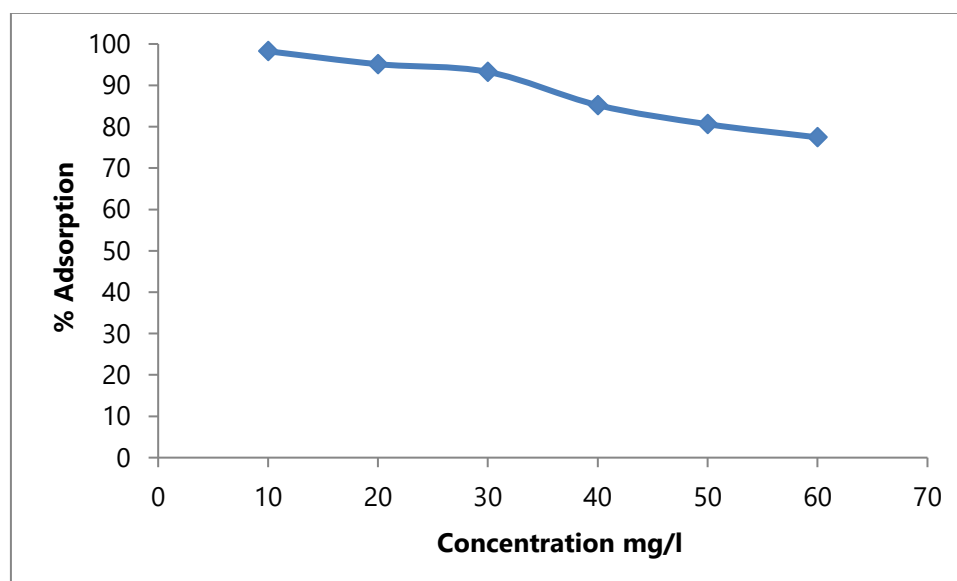


Figure 8. Effect of initial metal concentration on cadmium and cadmium removal efficiency

3.2. Adsorption Isotherm

In an adsorption process, as more and more metal ions get adsorbed on the solid surface a simultaneous desorption of the metal ions from the solid surface also starts to take place. With time, the rate of adsorption goes on decreasing and that of desorption goes on increasing. Consequently the rates of adsorption and desorption will attain an equilibrium state called adsorption equilibrium. At equilibrium, no change can be observed in the concentration of the solute on solid surface or in the bulk solution. At the end of the equilibration period, the aqueous phase concentration of adsorbate is measured and the adsorption equilibrium capacity is calculated using the mass balance expression.

$$q_e = \frac{V}{M} (C_o - C_e) \text{ ----- 7}$$

Where q_e is adsorption capacity at equilibrium (mg g^{-1}), C_o (mgL^{-1}), initial concentration of adsorbate, C_e (mgL^{-1}) equilibrium concentration of adsorbate, M (g), mass of adsorbent and V is volume of the solution.

Adsorption isotherm is needed to explain the adsorption process and to determine the adsorption efficiency of an adsorbent. Many sorption isotherm models are usually used to fit the adsorption data in order to obtain a linear regression data to predict the maximum adsorption capacity of the adsorbent. Langmuir and Freundlich models are the most widely used models in the case of the adsorption of metal ions with biosorbents.

3.2.1. Copper (II) adsorption isotherm

Copper (II) ions adsorption isotherm studies were carried out to determine an approximate estimation of adsorption capacity of adsorbent doses of: 0.5, 1, 2, 3, 4 and 5 g at initial metal ion concentration 40 mgL^{-1} , time 120 minute, pH4 and 180 rpm agitation speed (Table 2). Using Langmuir's equation to analyze copper adsorption isotherm, the graph shows the relation between C_e in the x axis and C_e/q_e in the y axis. On the other hand, the graph of Freundlich's equation shows the relationship between $\log C_e$ in the x axis and $\log q_e$ in the y axis.

Table 2. The results of Copper (II) adsorption isotherm Langmuir adsorption isotherm model for copper (II) ions

Dose of adsorbent (M) g	Residual concentration (C_e) mgL^{-1}	Adsorption capacity (q_e) mgg^{-1}	C_e/q_e	Log C_e	Log q_e
10	0.305	0.484	0.630	-0.516	-0.314

20	2.05	1.01	2.03	0.312	0.004
30	3.74	1.31	2.85	0.573	0,117
40	6.10	1.69	3.61	0.785	0.228
50	9.20	2.03	4.53	0.984	0.307
60	12.46	2.37	5.06	1.09	0.375

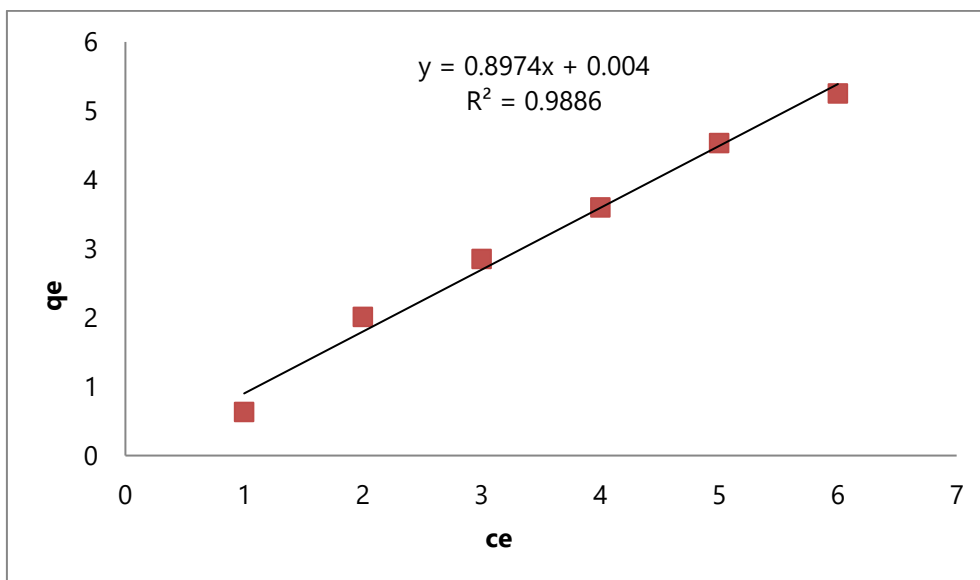


Figure 9. Langmuir adsorption isotherm for Cu (II) ions.

Langmuir model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules. In addition, the model assumes uniform energies of sorption on to the surface and no transmigration of the sorbate and is presented by the following linear equation.

$$q_e = q_m + bC_e / (1 + bC_e) \dots\dots\dots 8$$

The linear form Langmuir isotherm is given by the following equation (Langmuir, 1918).

$$C_e/q_e = C_e/q_m + 1/bq_m \dots\dots\dots 9$$

Plotting C_e/q_m against C_e , a straight line is obtained having a slope $1/bq_m$ and intercept $1/q_m$. (Figure 9). The maximum adsorption capacity (q_m) of the Orange peel calculated from the intercept was 4.115 mgg^{-1} . That is one gram of the orange peel can absorb 4.115 mg copper. The essential characteristic of the Langmuir isotherm may be expressed in terms of dimensionless separation parameter R_L , which is indicative of the isotherm shape that predicts whether an adsorption system is favorable or unfavorable (Juang, Wu, & Tseng, 1997). R_L is defined as:

$$R_L = 1 / (1 + bC_0) \dots\dots\dots 10$$

From the experiment, $R_L = 1/8968.61 = 0.0001$ which indicates a favorable adsorption. This means that Orange peel is a favorable adsorbent for the removal of Cu (II) ions.



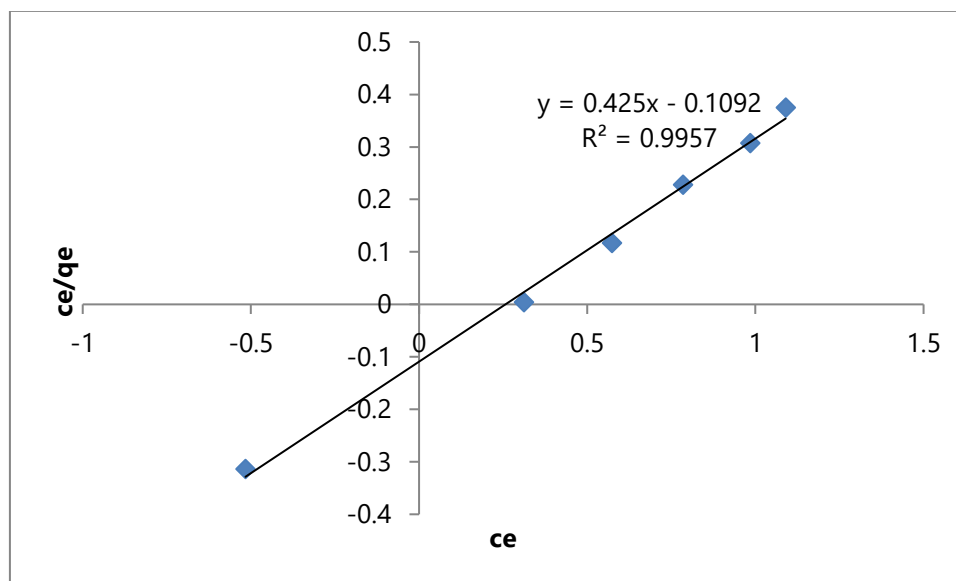


Figure 10. Freundlich adsorption isotherm for copper (II) ions

The Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous system. The Freundlich equation is expressed as:

$$q_e = K_f C_e^{1/n} \text{ ----- 11}$$

Where c_e is the solute equilibrium concentration and K_f and n are Freundlich constant related to adsorption capacity and adsorption intensity respectively. The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. For linearization of the equation, it can be written in logarithmic form.

$$\log q_e = \log K_f + 1/n \log C_e \text{ ----- 12}$$

Plotting $\log q_e$ versus $\log C_e$, a straight line was obtained with a slope of $1/n$ and intercept of $\log K_f$ (Figure 11). The value of Freundlich constant $1/n$ shows the concentration of solute adsorption. Besides, n value can indicate the capacity of adsorption and the adsorbent dose. If n is more than 1 ($n > 1$), it means the adsorbent can effectively adsorb the solute. From Freundlich equation the values of $1/n$ and n were obtained as 0.425 and 2.35, respectively. Since the values of $1/n$ lies between 0 and 1 and $n > 1$, it indicates that the Orange peel can adsorb copper effectively. The Langmuir model represents the experimental data less for Cu (II) ion having regression coefficient of 0.988 compared to 0.995 in Freundlich. However, since both values appeared relatively higher than 0.9, the copper adsorption on Orange peel was fitted with both adsorption isotherms i.e. each site of Orange peel can accommodate one molecule of copper ion or it is characterized by supporting surfaces of different affinity.

3.2.2. Cadmium (II) ions adsorption isotherm

The study was carried out by varying the concentration of the Cd (II) ions as 10, 20, 30, 40, 50 and 60 mgL⁻¹, time 120 minute, pH6 and 200 rpm agitation speed (Table 3). Using Langmuir's equation to analyze cadmium adsorption isotherm, the graph shows the relation between C_e in the x axis and c_e/q_e in the y axis. On the other hand, the graph of Freundlich's equation shows the relationship between $\log C_e$ in the x axis and $\log q_e$ in the y axis.

Table 3. The results of cadmium (II) adsorption isotherm

Dose adsorbent(M) g	Residual concentration (C_e) mgL ⁻¹	Adsorption capacity (q_e) mgg ⁻¹	C_e/q_e	Log C_e	Log q_e
10	0.9	0.455	1.98	-0.05	-0.34

20	2.72	0.862	3.15	0.43	-0.06
30	5.57	1.22	4.56	0.75	0.09
40	8.68	1.57	5.53	0.94	0.19
50	10.25	1.77	5.78	1.01	0.24
60	11.45	1.83	6.47	1.06	0.26

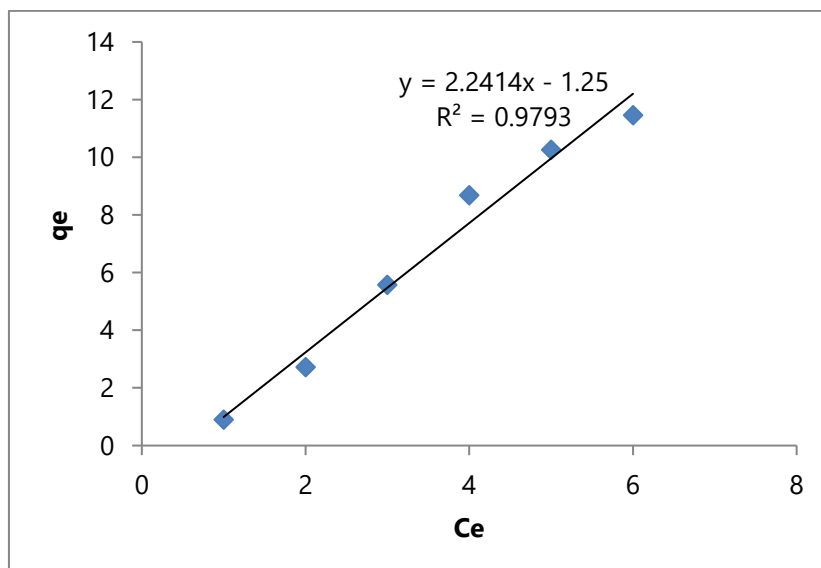


Figure 11: Langmuir adsorption isotherm of cadmium (II)

Plotting q_e against C_e , a straight line was obtained having a slope $1/bq_m$ and intercept $1/q_m$ (Figure 11). The maximum adsorption capacity (q_m) of the Orange peel calculated from the intercept was 2.45 mg/g. That is one gram of the Orange peel can adsorb 2.45 mg of cadmium. From the experiment, $R_L = 1/88 = -0.01$ which indicates a favorable adsorption. This means that Orange peel is a favorable adsorbent for the removal of Cd (II) ions.

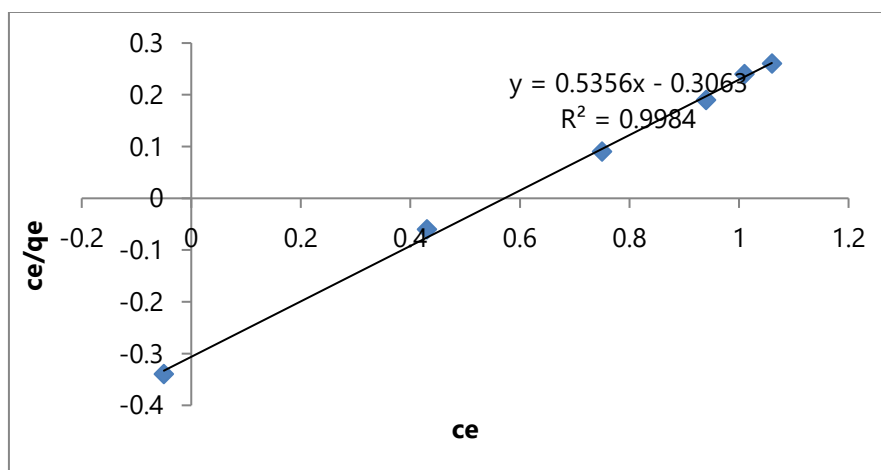


Figure 12 Freundlich adsorption isotherm for cadmium (II) ion

Plotting $\log q_e$ versus $\log C_e$, a straight line was obtained with a slope of $1/n$ and intercept of $\log K_f$ (Figure 12). The values of $1/n$ and n obtained from Freundlich's equation were 0.535 and 1.87 respectively. Since the values of $1/n$ lies between 0 and 1 and $n > 1$, it indicates that the Orange peel can adsorb cadmium effectively. The correlation coefficients (R^2) of orange peel in Langmuir equation exhibits less value than Freundlich (i.e. 0.979

and 0.998, respectively). However, in the broader perspective, both values appeared relatively higher than 0.9. Therefore, cadmium adsorption on Orange peel was fitted with both adsorption isotherms

Table 4. Langmuir and Freundlich constants for the adsorption of Cu (II) and Cd (II)

Metal ion	Langmuir				Freundlich		
	q_{\max}	b	R^2	R_L	K_f	1/n	R^2
Cu (II)	4.15	217.40	0.988	0.0001	0.78	0.425	0.995
Cd (II)	0.45	-1.78	0.979	-0.01	0.49	0.535	0.998

q_{\max} = maximum adsorption capacity (mg g^{-1}), b = constant related to binding energy, R^2 = correlation coefficient, R_L = separation factor, K_f = Freundlich adsorption capacity, n = Freundlich constant related to intensity of adsorption.

4.2.3. Comparison of adsorption capacity of Orange peel with other adsorbents

Table 5. Comparison of Adsorption Capacity of Orange peel for Cu (II) ion with other Adsorbents

Sorbent	q_{\max} (mg /g)	Reference
<i>Chlorella vulgaris</i> (1)	48.2	(Dönmez, Aksu, Öztürk, & Kutsal, 1999)
<i>Ascophyllum nodosum</i>	75.6	(Q. Yu, Matheickal, Yin, & Kaewsarn, 1999)
Grape stalks	22.1	(Machado, Santos, Correia, & Carvalho, 2003)
Orange peel	4.15	Present studies

Table 6. Comparison of adsorption capacity of orange peel for Cd (II) with other adsorbents The comparison of adsorbent capacity of Orange peel with other materials reported in the literature is given in

Sorbent	q_{\max} (mg /g)	Reference
Broad bean peel	147.71	(Benaissa, 2006)
Coconut copra meal	4.92	(Yuh-Shan Ho & Ofomaja, 2006)
Sugar beet pulp	17.20	(Reddad, Gerente, Andres, & Le Cloirec, 2002)
<i>Syzygium cumini</i> leaf powder	34.54	(K Srinivasa Rao, S Anand, & P Venkateswarlu, 2010)
Tree fern	16.30	(Y-Sh Ho & Wang, 2004)
Wheat bran	15.71	(Nouri, Ghodbane, Hamdaoui, & Chiha, 2007)
<i>Tectonagrandis</i> L.f	23.20	(Karanam Srinivasa Rao, Sashi Anand, & Paladugu Venkateswarlu, 2010)
Peanut hulls	5.96	(Brown, Jefcoat, Parrish, Gill, & Graham, 2000)
Grape stalk	27.88	(Martinez et al., 2006)
<i>Psidium guajava</i> / leaf powder	31.15	(K. Rao, S. Anand, & P. Venkateswarlu, 2010)
Orange peel	2.45	Present study

Table 4 and 5. Accordingly; the adsorption capacity of Orange peel for cadmium and copper obtained was less than most of the adsorbents from various industrial and low cost adsorbent listed in the table. Hence, Orange peel can be considered to be a viable adsorbent for the removal of Cu (II) and Cd (II) ions from aqueous solutions

4. Conclusion

In this work effectiveness of the Orange peel powder as bio sorbent for the removal of heavy metal ions (Cu (II) and Cd (II) ions) was studied. The effectiveness of parameters like pH, biomass dosage, contact time and initial metal ion concentration during the bio sorption process was noted. The desired pH for bio sorption was found to be 2.0 for copper and 6.0 for cadmium for the Orange peel under study. Higher bio sorbent dosages resulted in higher percent removal of Cu (II) and Cd (II) ions due to abundant availability of sorption sites and exchanging ions. The amount of the metal removed at optimum pH increased with increase in initial metal concentration. Adsorption data for wide ranges of adsorbent doses were treated by Langmuir and Freundlich isotherms. The adsorbent and adsorbates interaction followed both the Langmuir and Freundlich isotherms. Values of the equilibrium parameter (R_L) from Langmuir isotherm and n values from the Freundlich isotherm indicate that the adsorption process is favorable for both Cu (II) and Cd (II) ions from the aqueous solutions. Orange peel as an agricultural waste has negligible cost and has also proved to be an efficient adsorbent for the removal of the two metal ions studied (Cu (II) and Cd (II) ions from synthetic aqueous solution. Furthermore, this bio sorbent is of low cost; its utility will be economical and can be viewed as a part of a feasible waste management strategy.

Conflict of Interest: The author declare there is no conflict of Interest

Fund: Nil

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