

## Removal of Copper(II) and Cadmium(II) ions from Aqueous Solutions Using Banana Peels and Bentonite Clay as Adsorbents

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### Abstract

Adsorption removal of Cu(II) and Cd(II) from aqueous solution using low-cost banana peels (a food waste) and bentonite clay (natural resource), was investigated. The adsorption process was studied in a batch scale at mean operation parameter which were pH, adsorbent particle size, adsorbents dosages, and initial concentrations of metal ions. All experiments were conducted at room temperature. Langmuir and Freundlich adsorption isotherm models were achieved to describe the quantitative uptake of Cu(II) and Cd(II) ions by adsorbates. The results show that the maximum adsorption removal reach to 80% and 99.5% for Cu(II) on to banana peels and bentonite respectively and 77 % and 98% for Cd (II) onto banana peels and bentonite respectively at optimum operating conditions: pH 5, particle size 75 $\mu$ m, adsorbent dosage 2 g/100ml and metal concentration 5 mg/L. The equilibrium adsorption data for Cu(II) and Cd(II) were better fitted to Freundlich adsorption isotherm model than Langmuir.. The study concludes the use of banana peels as a food waste and bantonite as a natural adsorbent for removing Cu (II) and Cd(II) from aqueous solution was effective. Thus offering a low cost material show potential use it to remove heavy metals.

**Keywords:** Banana peels; Bentonite; Adsorption; Copper; Cadmium; Isotherms.

### إزالة أيونات النحاس والكاديوم من المحاليل المائية باستخدام قشور الموز والبنطونايت كمادة ممتزة

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### ملخص البحث

تمت دراسة إمكانية إزالة أيونات كل من النحاس والكاديوم من المياه الصناعية باستخدام مادة ممتزة متوفرة محليا وهي قشور الموز ومادة ممتزة من الطبيعة وهي البنطونايت. أجريت التجارب بنظام الدفعة الواحدة وبظروف تشغيلية متغيرة لكل من pH المحلول وحجم دقائق المادة الممتزة وجرعة المادة الممتزة وتركيز المعادن التي يراد امتزازها، التجارب أجريت بدرجة حرارة الغرفة. تم استخدام معادلتى لانكبير وفريندلش لتمثيل نتائج امتزاز كل من النحاس والكاديوم. أعلى نسب إزالة وصلت الى 80% و99.5% للنحاس باستخدام قشور الموز والبنطونايت على الترتيب، و77% و98% للكاديوم باستخدام قشور الموز والبنطونايت على الترتيب. أفضل النتائج كانت عند pH 5 وحجم دقائق الممتز 75 مايكروميتر وجرعة 2 غم/100مل وت ركيز معدن 5 ملغم/لتر، التجارب كانت أكثر مطابقة لمعادلة فريندلش مما هي لمعادلة لانكبير. الدراسة أثبتت كفاءة كل من قشور الموز والبنطونايت في إزالة كل من النحاس والكاديوم من المياه الصناعية مع التوصية باستخدام المواد المتوفرة محليا واقل كلفة مادامت لها الكفاءة في إزالة المعادن الثقيلة. **كلمات دالة:** قشور الموز، البنطونايت، الامتزاز، النحاس، الكاديوم، التوازن.

## 1. Introduction

Heavy metals are generated from industrial wastewater with various toxic. Because the heavy metals can not be biodegraded, so they have accumulating characteristics in nature and they have become hazardous for living organisms especially when they exceed the specific limits. Among the heavy metals, copper and cadmium is the major available type of heavy metal in the aquatic environment. The excess copper compound in the body has a gastrointestinal effects<sup>[1]</sup>, and cadmium recognized toxic and posing a widespread threat to humans and wildlife, human carcinogen, also has a kidney effect<sup>[1]</sup>. During the last few decades, the sustainable removal of heavy metals from water and wastewater has become a prime concern and a major challenge for scientists. Owing to the toxic and adverse effects of heavy metals, most industries are advised to treat wastewaters systematically so that the metal contents can be minimized in their wastes. Various conventional treatments have been applied for removing heavy metals such as chemical precipitation<sup>[2]</sup>, ion exchange<sup>[3]</sup>, filtration<sup>[4]</sup> and electrochemical treatment<sup>[5]</sup> but most of these methods are only suitable for large scale treatments and incur high cost to be practiced. Generally, all these treatments lead to certain disadvantages such as incomplete removal of heavy metals, high-energy requirements and production of toxic sludge<sup>[6]</sup>. Extensive studies have been undertaken for the development of more effective methods in removing metal pollution, so the adsorption is found to be the most effective process over other techniques. Activated carbon (AC) is used for effective adsorption. However, AC sometimes has a cost effect. Moreover, it becomes not an economic process if the AC needs to modify<sup>[7]</sup>. High cost of activated carbon encourages using lower cost and/or waste materials as adsorbent for various pollutant removals from the aqueous environment. Numerous approaches have been studied in recent years in order to find an economic adsorbents for water treatment and heavy metals removing<sup>[8]</sup>. Bentonite clay from natural resources can be used as an adsorbent for the removal of heavy metals from aqueous systems<sup>[9]</sup>. Bentonite may be used for elimination of heavy metal pollution from wastewater since it is a low-cost, abundant and locally available adsorbent<sup>[10]</sup>. Also different bioadsorbents are developed i.e food waste or agro- waste such as the rice bran has been found to be a very effective adsorbent for the efficient removal of Pb(II) from water<sup>[11]</sup>. Orange peel, sawdust and bagasse are excellent adsorbents for the removal of copper from aqueous solution.<sup>[12]</sup> The adsorption of copper from aqueous solution using papaya seed as the low-cost adsorbent was investigated in batch process<sup>[13]</sup>. Myrtus-communis was proved successful for removal of Cu (II), Pb(II), Mn(II), and Co (II) ions from waste water<sup>[14]</sup>. The adsorption performance of Cu<sup>+2</sup>, Pb<sup>+2</sup> and Zn<sup>+2</sup> on modified orange peel are significantly affected by pH and metal concentrations<sup>[15]</sup>. Therefore bentonite clays and dried banana peel are used in this study to investigate the removal of copper and cadmium from wastewater synthesized in the laboratory. The experiments were carried out by batch process.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1 Adsorbents

Banana peels was collected from the local market in Baghdad, cut into small pieces (about 3 cm<sup>2</sup>), washed with tap water and distilled water three times. The wetted banana peel was dried in oven at 75°C for 24 hours. The dried banana peel was grounded into powder and sieved to the desired particle size for experimental uses<sup>[16]</sup>. A local bentonite clay type Na-bentonite, was obtained from the Geological Survey and mining company. Table (1) shows the chemical composition and specific surface area of banana peels and bentonite.

**Table(1) banana peels and Na-bentonite chemical composition and BET surface area.**

Banana peel		bentonite	
Composition	% mass	Composition	% mass
-----		SiO <sub>2</sub>	56.9
-----		Al <sub>2</sub> O <sub>3</sub>	25.0
-----		TiO <sub>2</sub>	1.6
Fe	0.061	Fe <sub>2</sub> O <sub>3</sub>	8.9
Ca	1.920	CaO	1.5
Mg	7.620	MgO	1.2
Na	2.430	Na <sub>2</sub> O	1.5
K	7.810	K <sub>2</sub> O	1.0
Others	80	Others	1.4
BET surface area	13 m <sup>2</sup> /g	BET surface area	56.6 m <sup>2</sup> /g

### 2.1.2 Adsorbate

The stock solution 1000 mg/L of Cu(II) and Cd(II) ions were prepared by dissolving 3.51 g of pure salt CuSO<sub>4</sub>.5H<sub>2</sub>O and 2.036 g of CdCl<sub>2</sub>.2H<sub>2</sub>O in 1L of deionised water and practiced for all experiments with required dilution.

## 2.2. Methods

### 2.2.1 Study of pH

To study the effect of pH on Cu(II) and Cd(II) adsorption onto banana peel and bentonite, dosage of banana peel and bentonite were kept constant at 2g/100 ml, and particle size 150 µm, while varying the pH of the samples using 0.1M H<sub>2</sub>SO<sub>4</sub> and 0.1M NaOH between (2 to 8). Each of Cu(II) and Cd(II) concentrations were 5 mg/L for all solutions during the experiment. Adsorption studies were carried out at room temperature. There was shaken for 3 hours with 150 rpm (this speed was able to mix and reaches to equilibrium), at room in the 100 ml flask volume and left still for 24 h<sup>[16]</sup>. Optimum pH value helps to make the study of effect of other factors, more easier.

### 2.2.2 Study of particle sizes

Banana peels had been sieved after it was grounded with standard sieves to five particles sizes of 600, 425, 300, 150, and 75 µm. From each graded sizes of banana peels was added to five sets with 100 ml of distilled water, it was carried out by shaking 600, 425, 300, 150 and 75 µm with 2g of banana peels with 100 ml aqueous solution for each of Cu and Cd adsorbates with concentrations 5 mg/L at pH 5 in different glass bottles in a shaking thermostat at a constant speed of 150 rpm for 3 hours and left still for 24 h. The water samples were then filtered with filter paper and analyzed. The same procedure was done with bentonite clay.

### 2.2.3 Study of adsorbent

The impact of the adsorbent amount on the equilibrium adsorption for each of Cu(II) and Cd(II) were investigated with banana peels and bentonite of 0.5, 1, 2, 3 and 4 g in six sets

of 100 ml water, which contained 5 mg/L of Cu(II) and Cd(II) concentrations each, at pH 5 and particle size 75 $\mu$ m. The samples were shaken at speed 150 rpm at room temperature for 3 hours and were left for 24 hours before the water samples filtered and analyzed in terms of Cu(II) and Cd(II). The same procedure was done with the bentonite as an adsorbent.

### 2.2.4 Equilibrium Studies of Cu(II) and Cd(II) Adsorption

The need to apply the Langmuir and Freundlich adsorption isotherms, a series of solutions containing different initial concentrations of Cu and ions (2.5, 5, 10, 15, 20 and 30 mg/L) were prepared and employed in the batch adsorption studies at room temperature and optimum conditions obtained previously. They were shaken for 3 hours with speed 150rpm at room temperature and left still for 24 h. Water samples were filtered and analyzed. The same procedure was done with the bentonite as an adsorbent.

## 3. Analysis, Calculations and Models

GEMMY orbit shaker, model VRN-480, Germany was used for shaking process. Water samples were filtered by Whatmann filter GF/C (1.2 $\mu$ m). The pH was measured by pH meter 3110, WTW, Germany. The concentrations of Cd(II) and Pb(II) ions in the solutions before and after equilibrium were determined by AA-6200 Atomic absorption flame emission spectrometer (Shimadzu, Japan). The pore structure and images of the powdered samples before and after Cu(II) and Cd(II) adsorption were observed using a scanning probe microscope (CSPM). Fourier transform infrared spectroscopy (FTIR) IR Prestige-21 (Shimadzu, Japan) was used to identify the different chemical functional groups present in the FL. FTIR, analyses were also used to determine the functional groups which are responsible for the metal binding with the adsorbents. The analysis was carried out using KBr, and the spectral range varies from 4,000 to 400  $\text{cm}^{-1}$ . The surface area was performed in a Micromeritics surface area analyzer (model ASAP 2020, Micromeritics) using the (BET Brunauer-Emmet-Teller) method with an average particle diameter of 141.84 nm. The removal efficiency (R%) of Cu(II) and Cd(II) ions was calculated for each run by the following expression:

$$R \% = \left( \frac{C_o - C_e}{C_o} \right) * 100 \quad (1)$$

Where  $C_o$  and  $C_e$  are the initial and the equilibrium concentrations of metal ions in the solution. The equilibrium adsorptions of Cu(II) and Cd(II) by adsorbents were calculated as follows<sup>[17]</sup>:

$$q_e = \frac{(C_o - C_e) * V}{M} \quad (2)$$

Where,  $q_e$ , the equilibrium adsorption capacity (mg/g);  $C_o$  and  $C_e$  are the initial and the equilibrium concentrations of metal ions in the solution, respectively (mg/L).  $V$  is the volume of solution (L), and  $M$  is the adsorbent mass (g).

## 4. Results and discussion

### 4.1 FTIR analysis

FTIR spectroscopy was performed to characterize the chemical functional groups of banana peels and bentonite. These spectra were obtained from scanning in the range of 400-4000 $\text{cm}^{-1}$ . The IR spectrums are shown in Fig. 1 ( upper black line) for banana peels. The bands in the region of 3390.8  $\text{cm}^{-1}$  was attributed to O-H stretching, those at 2927.94 and 2854.65  $\text{cm}^{-1}$  to C-H stretching, and the bands appearing at 1728.22 , 1712.79 and 1612.49 $\text{cm}^{-1}$  was attributed to the C=O, while , at 1431.18 to 1199.72  $\text{cm}^{-1}$  attributed to C-O stretching, and the bands at 1068.56 to 925.83  $\text{cm}^{-1}$  attributed to O-H . The N-H deformation band was found at 891.11, 817.82  $\text{cm}^{-1}$ . The significant shifts of these specific peaks Fig.1 ( lower red line) after the metal ion absorption denoted that chemical interactions between the metal ions and the groups occurred on the biomass surface. The band of banana peel shifted to 317.86  $\text{cm}^{-1}$ , and to 2920.23  $\text{cm}^{-1}$  indicating that hydroxyl, carboxyl and amine groups were involved in the biosorption. The spectra of at 1728.22 become 1735.92  $\text{cm}^{-1}$ , and a band of banana at 1543.05 and 1519.91  $\text{cm}^{-1}$  appeared, which would result from the complexation of metal ions with the functional groups from protein. These results indicated that carboxyl, hydroxyl and amine groups on the banana peel surface were interested in the adsorption of the metal ions<sup>[16]</sup>.

Fig.2 ( upper black line) shows the FTIR spectra of the bentonite sample as well as the saturated samples (lower red line). The sharp bands at 3630.03 and 3525.88  $\text{cm}^{-1}$  were attributed to the OH group (Al-OH and Si-OH ). The peak at 3425.58  $\text{cm}^{-1}$  was attributed to OH . Peak at 1435.04 was assigned to OH deformation mode of water. The stretching vibration of Si-O group due to tetrahedral environment of the inner layer was found at 1114.86 and 1037.7  $\text{cm}^{-1}$ . The peak of isomorphic substitution of Al-Al-OH type due to internal environmental of the octahedral layer was found at 918.12 , stretching at 875.68  $\text{cm}^{-1}$  was assigned to Al-Fe-OH., the peak at 833.25  $\text{cm}^{-1}$  was assigned to Al-Mg-OH, the other vibration at 798.53 and 574.97  $\text{cm}^{-1}$  are assigned to Si-O-Al bands stretching.<sup>[17]</sup> New bands appeared at 1797.66, 1026.13, 779.24 and 690.52  $\text{cm}^{-1}$  which would result from the complication of Cu (II) and Cd (II) with the functional groups.

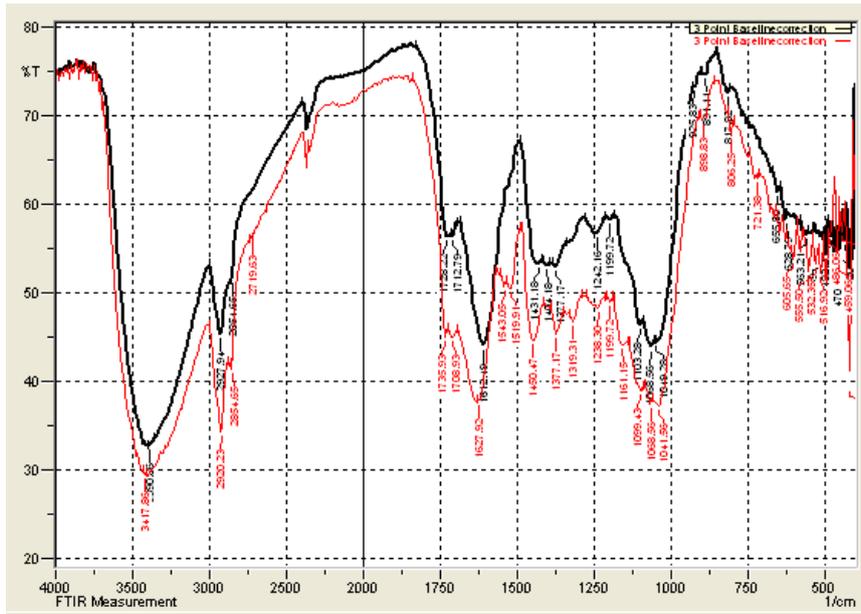


Fig.(1) FTIR of virgin (upper black) and saturated banana peels (lower red).

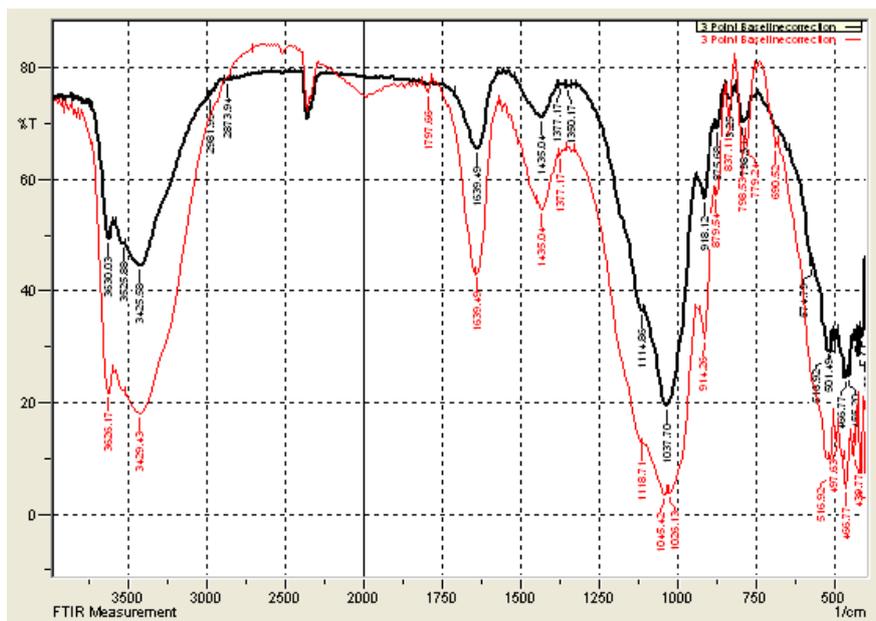


Fig.(2) FTIR of virgin (upper black) and saturated bentonite (lower red).

#### 4.2 BET surface area

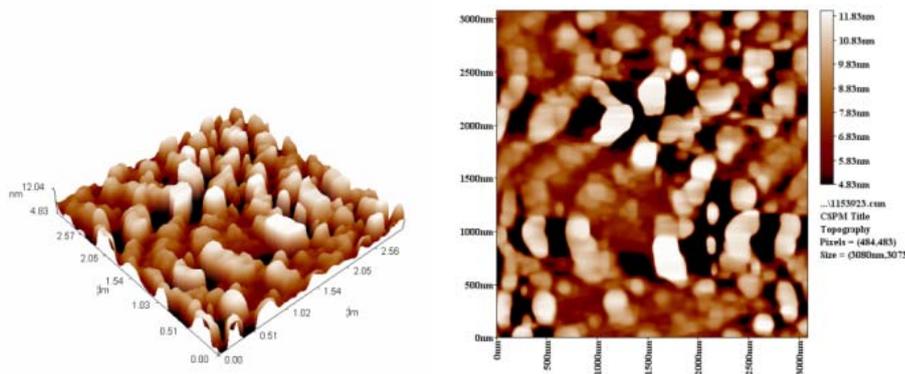
The bentonite clay has a silica based materials in noticeable surface area (table 1) if it compared with banana peels particle (low surface area) because it is a self character of carbonaceous materials.

### 4.3 Scanning probe microscope

The CSPM (scanning probe microscope), fig.3, 4, 5 and 6 , characterized that banana peels and bantonite clay have amorphous and granular surfaced. The electron microscope, also, revealed that the particles are heterogeneous, rough surface, its surface exhibits a micro-rough texture, which can promote the adhesion of copper and cadmium. .In comparison, between CSPM images for surface roughness analysis (fig.3, 4, 5 and 6 ),brings to light the manifest differences between the results before and after adsorption, this means banana peels and bentonite clay were free of any Cu(II) and Cd(II), but, after the experiment had been achieved, the powder had a surface partially covered by heavy metals (table 2).

**Table.(2) Banana peel and bentonite characteristics before and after adsorption by CSPM.**

Banana peel		
	Before	After
Sa(roughness av.)	1.92 nm	0.192 nm
Ssk(surface skewness)	0.0981	0.345
Ten point height	7.5 nm	1.24 nm
Sar(surface area ratio)	0.211	0.011
Sk(core roughness depth)	6.14 nm	0.405 nm
Bentonite		
Sa(roughness av.)	5.42 nm	1.7 nm
Ssk(surface skewness)	0.228	0.236
Ten point hight	23.2 nm	7.31 nm
Sar(surface area ratio)	1.35	0.179
Sk(core roughness depth)	19.6 nm	6.1 nm



**Fig. 3. Scanning probe microscope for banana peels before adsorption.**

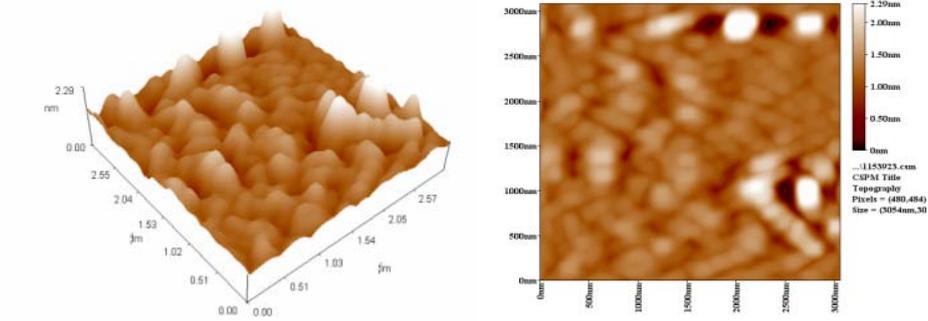


Fig. 4. Scanning probe microscope for banana peels after adsorption.

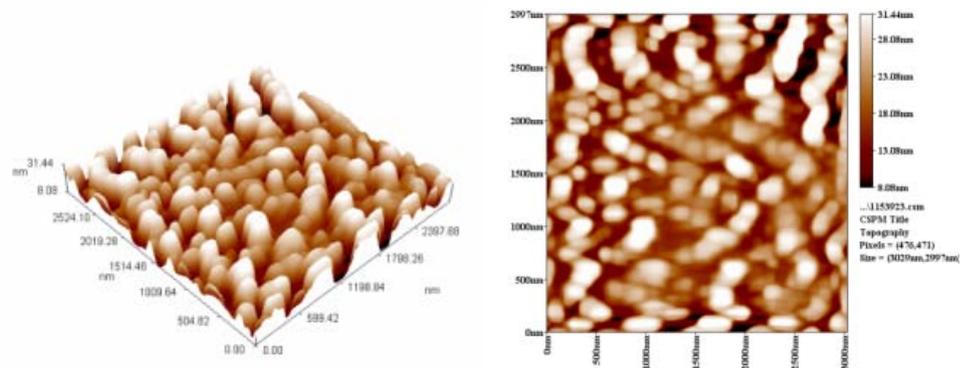


Fig. 5. Scanning probe microscope for bentonite before adsorption.

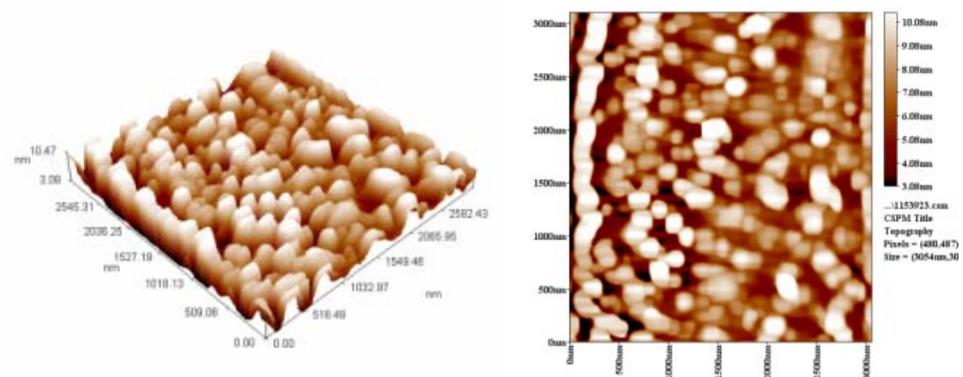
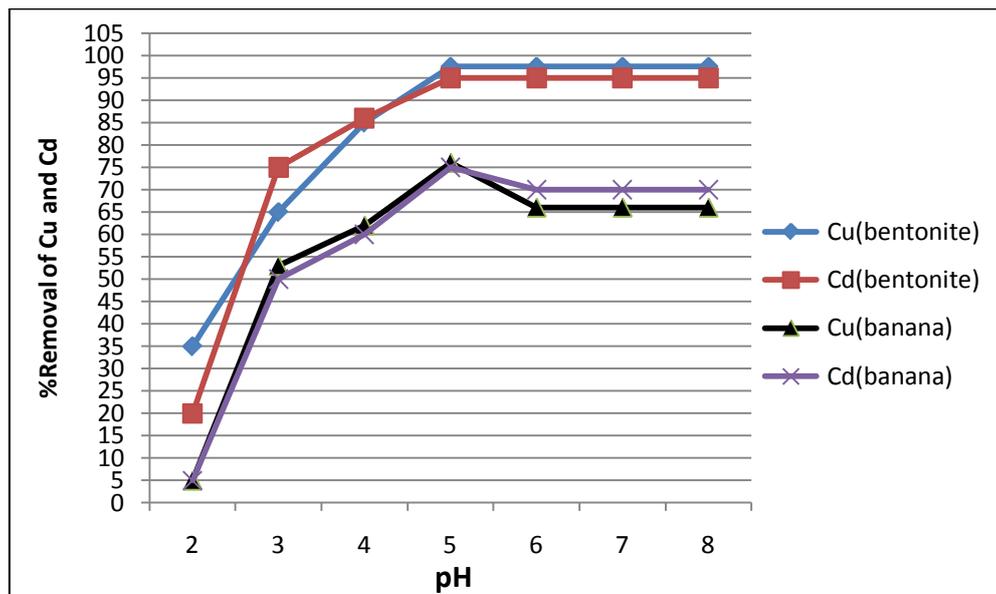


Fig. 6. Scanning probe microscope for bentonite after adsorption.

#### 4.4 Effect of pH

pH is an important parameter that control the adsorption process of metal onto any adsorbent. Accordingly, different pH values were studied (2-8) with constant banana peels dosage 2 g, particle size 150  $\mu\text{m}$  and metals concentration 5 mg/L. From fig.(7) , Cu(II) adsorption onto banana peels increased when pH increased from 2 to 5 , with the following percentage removing (from 5 to 76%),the maximum value was (76 %) at pH 5,after that constant percentage removal was obtained with pH (6-8)and it did not exceed 66% .The same results was obtained when Cu(II) was treated with modified orange peel<sup>[15]</sup>.The adsorption rate for Cd(II) was increasing by pH increasing from 2 to 5 sequentially , from 5 to 75 %,then the adsorption rate for the cadmium started to decrease with pH( 6- 8) to 66 %and became constant. Similar trend was reported for the adsorption of Cd(II) onto banana peels<sup>[18]</sup>. Fig (7) reveals the effect of pH ranges on the adsorption rate for Cd(II) on banana peels. After the acidic condition with high degree of protonation of the adsorbent, pH increased leading to reduce the pronation, therefore the adsorption decreased. <sup>[19]</sup>.The adsorption started to decrease above pH 6, because Cu(II) and Cd(II) started precipitating <sup>[20]</sup>.



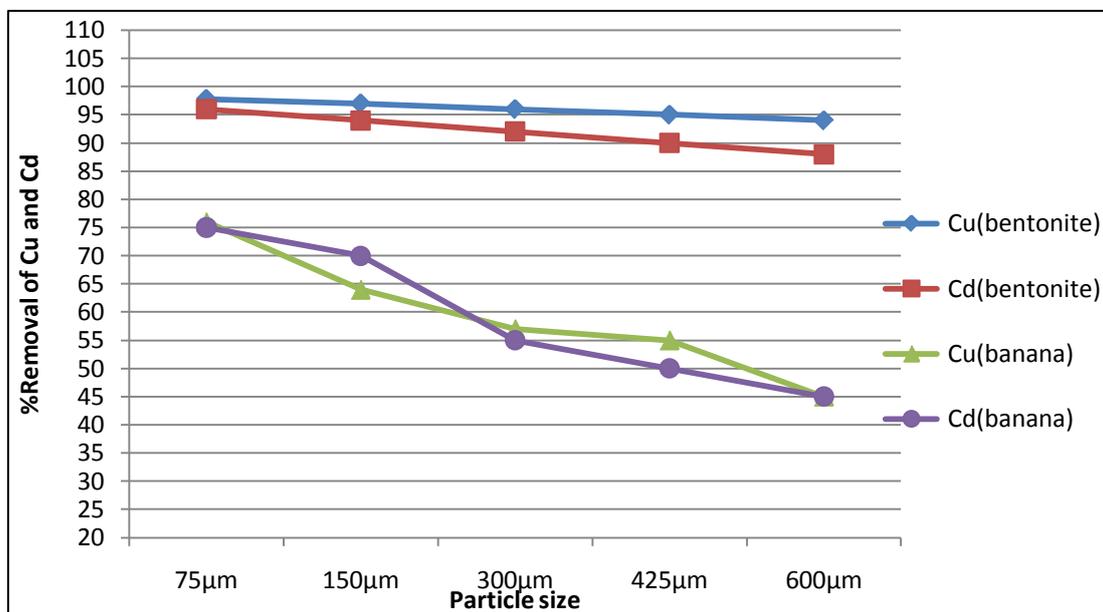
**Fig. 7. Effect of pH on the adsorption of Cu(II) and Cd(II) by banana peels and bentonite. Initial concentration 5 mg/l, adsorbent dosage 2 g/100 ml, particle size 150  $\mu\text{m}$ .**

The previous optimum conditions were used to evaluate the adsorption of Cu(II) and Cd(II) onto bentonite with pH variation , fig(7)shows the percentage removal of Cu(II) from simulated wastewater when pH varied from 2 to 8,the results were(35, 65, 85, 97, 97, 97and 97%), for Cd(II) were (20, 75, 86, 95, 95, 95 and 95%), the percentage removal rate was increasing when pH was increasing to reach the maximum value at pH 5 and keep constant value(97%)for Cu(II),and(95%) for Cd(II) (fig.7).This behavior explained as follows: at low

pH the solution has high  $H^+$ , preventing the metal adsorption on to bentonite, then while the pH was raising,  $OH^+$  was also raising to enhance Cu(II) and C(II) ions to adsorb on to adsorbent ,after that when pH increase, NaOH react with free metal ions which going to precipitate as a hydroxide<sup>[21]</sup> .Similar results were obtained by Lucia Helena Garofalo Chaves et.al,<sup>[21]</sup> and SevilVeli et.al,<sup>[10]</sup>.

#### 4.5 Effect of particle size

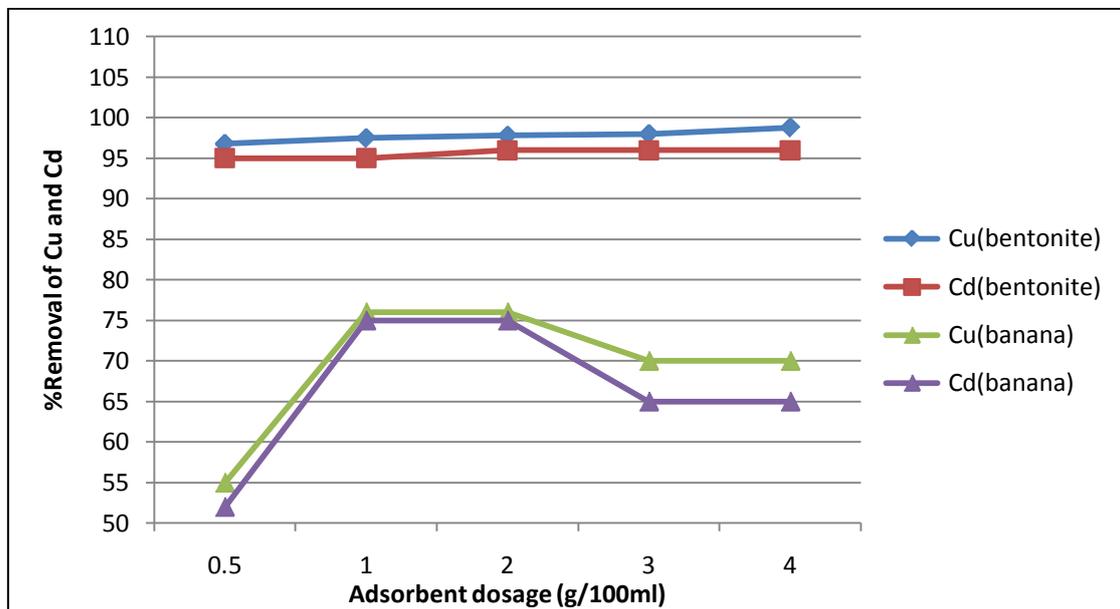
The effect of particle size was studied, experiments were carried out at room temperature, pH 5, banana peels and bentonite dosage 2 mg and Cu(II) and Cd(II) concentration 5 mg/l, for each of the following particle sizes (600,425,300,150 and 75  $\mu m$ ) in 100 ml volume of solution. For banana peels, fig(8) indicates that the percentage removal of Cu(II) and Cd(II) increased by decreasing the particle sizes. The percentage removal of Cu(II) increased as follows 45, 55, 57, 64 and 76% when decreasing particle sizes (600,425,300, 150 and 75 $\mu m$ ) respectively. As well as, the percentage removal of Cd(II) increased( 45, 50, 55, 70, and 75%) with decreasing particle sizes (600,425,300,150,and 75 $\mu m$ ) respectively. However there was no significant percentage removal within the particle size 425 to 75  $\mu m$ . These results are consistent with the results obtained from similar studies<sup>[16]</sup>. Again, for bentonite adsorbent ,fig(8) reveals that the removal efficiency of Cu(II) and Cd(II) were increased by decreasing the particle sizes. The percentage removal of Cu(II) increased (94, 95, 96, 97and 97.5%) when the particle sizes decreased( 600,425,300,150,and 75 $\mu m$ ) respectively. Moreover, the percentage removal of cadmium increased by (88, 90, 92, 94.6 and 96%) when decreasing particle sizes (600,425,300, 150 and 75 $\mu m$ ) respectively. This because of the inversely relation between the particle size and the surface area, when the particle size decreases, the active sites on the adsorbent increase, so the metal uptake increases<sup>[9]</sup>.



**Fig. 8. Effect of particle size on the adsorption of Cu(II) and Cd(II) by banana peels and bentonite. Initial concentration 5 mg/l, adsorbent dosage 2 g/100ml and pH 5.**

#### 4.6 Effect of adsorbent dosage

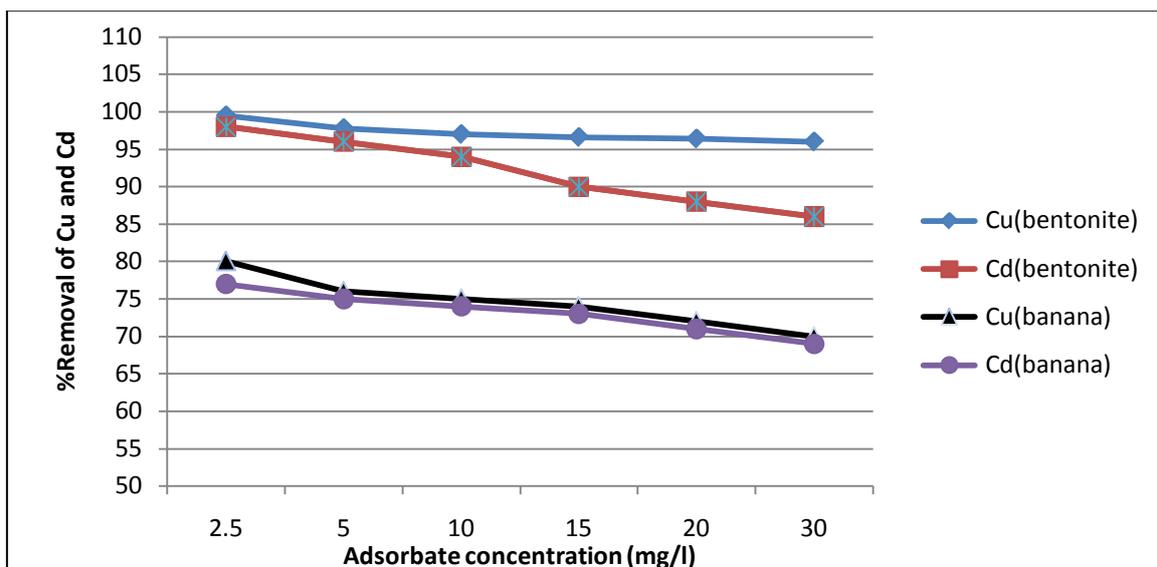
The effect of adsorbent dosage on banana peels and bentonite to remove each Cu(II) and Cd(II) from aqueous solutions was investigated. The adsorbent dosages were 0.5 ,1, 2, 3 and 4 g, have 150  $\mu\text{m}$  particle size, were added each to five sets of flask 100 ml, 5 mg/l metal concentration and pH 5. Results in fig.(9) obtained from this study to describe the percentage removal of Cu(II) which increases from 55 to 76 %, when the dosage of banana peels was increased from 0.5 to 2 g/100 ml and from (52 to 75% with dosages from 0.5 to 2 g/100 ml for Cd(II), the increasing of adsorption percentage with the dosage increasing due to the availability of active and surface area of adsorbent <sup>(9)</sup>. While the percentage removal decreased down to 70% when the dosage of Cu(II) were 3 and 4 g/100 ml and 65% for Cd(II), this because of less ratio of metal per unit mass of adsorbent, so, any addition of adsorbent made no differences in percentage removal. Similar results are also reported when the adsorbent dosage was studied <sup>[12],[22]</sup>. The study was going on in order to determine the effect of bentonite dosage on the adsorption rate of Cu(II) and Cd(II), solutions with previous conditions. The results are shown in fig(9) for Cu(II) and Cd(II) removal, it is seen that the adsorption efficiency increases as the bentonite clay amount increases, because of the increasing of surface area compared with banana peels. With bentonite clay dosage 0.5 g/100 ml, the removal efficiency for Cu(II) was 96.8% and for Cd(II) 95%, then the percentage removal reached 98.8 % for Cu(II) and 96% for Cd(II) with 4 g/100ml. The percentage removal of Cu(II) and Cd(II) by bentonite clay was studied with similar results. <sup>[9],[10]</sup>.



**Fig. 9. Effect of adsorbent dosage on the adsorption of Cu(II) and Cd(II) by banana peels and bentonite. Initial concentration 5 mg/l, pH 5 and particle size 75  $\mu\text{m}$ .**

#### 4.7 Effect of initial metal ions concentration

Initial concentration of metal ions can affect the metal percentage removal. In this study the initial concentrations of Cu(II) were varied (2.5, 5, 10, 15, 20 and 30 mg/l), at pH 5 using 2g/100 ml banana peels and 75  $\mu$ m particle size. Results obtained show that the increase of Cu(II) concentration from 2.5 to 30 mg/L, decreased the percentage removal from 80 to 76%. In comparison with Cu(II) ions adsorption, Cd(II) ions analysis revealed the same indication, the percentage removal was decreased with increase in metal ions concentration from 2.5 to 30 mg/l by 77 to 69% respectively, (fig.10). However uptake of Cu(II) and Cd(II) by unit weight of the adsorbent was increasing. The amount of 2 g of bentonite clay was added to 100 ml of aqueous solutions of Cu(II) and Cd(II) with the initial concentrations 2.5, 5, 10, 15, 20 and 30 mg/l, the suspensions were under constant pH 5 and particle size 75  $\mu$ m. The results obtained are shown in fig. (10). The curve shows that the maximum removal efficiency of Cu(II) by bentonite is 99.5%. This percentage of Cu(II) removed was significantly decreased with the initial concentration increasing, but with slight differences between them. Moreover, the percentage removal of Cd(II) by bentonite clay was varying inversely with the initial concentration of cadmium. Fig(10) revealed that the removal efficiency changed from 98% to 88% when the initial ion concentration increased from 2.5 to 30 mg/l. These results agree with the results of the adsorption of Cu(II) and Cd(II) on to natural bentonite<sup>[21]</sup>. Similar studies proved that the relation between the initial concentrations and the removal efficiency takes inverse direction, under optimum conditions, and constant adsorbent dosage, this can be explained by the fact that the adsorbent particles have a limited number of active sites from which they can adsorb a certain amount of metal concentration. Moreover, since the adsorbent dosage is constant there is a limited metal concentration coming into contact with the adsorbent particles, even if the metal concentration coming higher<sup>[12][23]</sup>.



**Fig. 10.** Effect of initial concentrations on the adsorption of Cu (II) and Cd (II) by banana peels and bentonite. Adsorbent dosage 2 g/100ml, pH 5 and particle size 75  $\mu$ m.

## 5. Adsorption Equilibrium Study

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. Adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate. The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for the design purpose. Two adsorption isotherms were used to fit the equilibrium data Langmuir and Freundlich.

### 5.1. Langmuir Isotherm

The Langmuir isotherm is based on assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, the energy of adsorption is constant, and there is no transmigration of the adsorbate in the plane of the surface<sup>[24]</sup>. The Langmuir equation is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $q_m$  is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg/g) and  $K_L$  is the Langmuir constant (L/mg) related to energy adsorption capacity. Langmuir equation can be linearized by the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

The values of  $q_{max}$  and  $K_L$  were computed from the slope and intercept of the Langmuir plot of  $C_e/q_e$  versus  $C_e$ . The Langmuir parameters  $q_{max}$  and  $K_L$  provide useful information regarding the equilibrium sorption process behavior. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term ( $R_L$ ) to determine high-affinity adsorption<sup>[25]</sup>.  $R_L$  was calculated as follows:

$$R_L = \frac{1}{1 + K_L C_o} \quad (5)$$

Where  $C_o$  is the initial metal concentration (mg/L) and  $R_L$  values indicate the shape of the isotherm. The nature of the adsorption process to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).

The linear plot of the Langmuir isotherm for Cu(II) and Cd(II) adsorption and the calculated parameters along with regression coefficients are shown in fig.(11, and 12) and Table (3 and 4) respectively. From tables. Maximum adsorption capacity,  $q_m$ , for complete monolayer coverage are found 9.3 and 8.34 mg/g for Cu and Cd, respectively onto banana peels, and 22.8 and 27.8 mg/g for Cu, Cd respectively onto bentonite.  $R_2$  values were between 0 and 1,  $R_L$  values obtained are also listed in Tables (3 and 4). All the  $R_L$  values for the adsorption the metals onto banana peels and bentonite clay show that the adsorption process favorable.  $K_L$  is the adsorption constant related to the affinity of binding sites (L/g) and lower value of  $K_L$  (0.01805 and 0.0217 L/g) for adsorption on to banana peels indicate that the particles radius of banana peel were small toward adsorption. However, good results were obtained for  $K_L$  when bentonite was used (0.828 and 1.064 L/g).

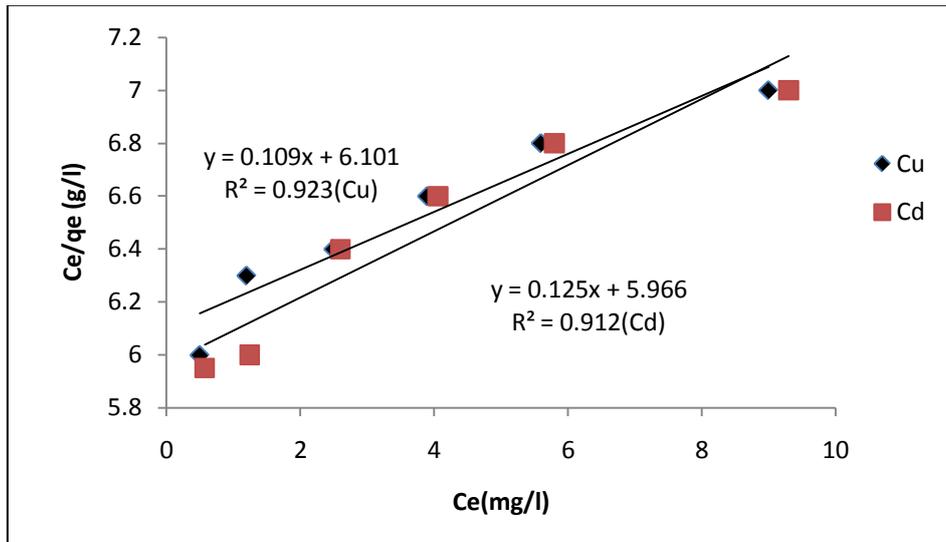


Fig. 11. Langmuir adsorption models for interactions of Cu (II) and Cd(II) on banana peels.

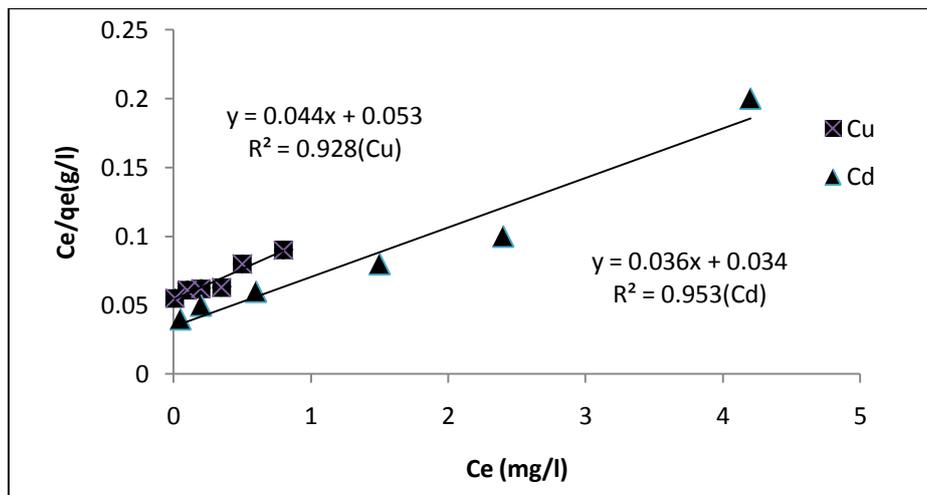


Fig. 12. Langmuir adsorption models for interactions of Cu(II) and Cd(II) on bentonite.

### 5.2. Freundlich Isotherm

Freundlich isotherm is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents. The Freundlich equation form could be written as follows [26]

$$q_e = K_f C_e^{1/n} \quad (6)$$

$q_e$  mass of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of adsorbate (mg/l),  $K_f$  and  $n$  are the Freundlich constants related to the adsorption capacity and adsorption intensity. The constants  $K_f$  and  $1/n$  were calculated from the intercept and slope of the plot of  $\ln q_e$  versus  $\ln C_e$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (7)$$

Fig(13 and 14) reveal the linear plot of Freundlich isotherm plot for adsorption of copper and cadmium onto selected adsorbents. The calculated parameters were tabulated in Tables (1 and 2). The Freundlich isotherm model was found best fitted with experimental data as it poses higher  $R^2$  value (0.998, 0.992, 0.998 and 0.996) respectively (tables 3 and 4).  $K_f$  is a Freundlich constant that shows the adsorption capacity on heterogeneous sites with non-uniform distribution of energy level. The adsorption intensity given by the Freundlich coefficient ( $1/n$ ) is smaller than the unity, indicating the favorable adsorption<sup>[25]</sup>. These results indicate the Freundlich equation represents a better fit than Langmuir when experimental data obtained from banana peels and bentonite. The Langmuir equation is shown a homogeneous adsorption, while Freundlich equations is demonstrated a heterogeneous adsorption. The correlation coefficients are shown in Tables 3 and 4. The  $R^2$  value of the Freundlich representing to be good adsorption of copper and cadmium on banana peel and bentonite better than the Langmuir plot, this indicated that the heterogeneous adsorption occurred on surfaces<sup>[27],[28]</sup>.

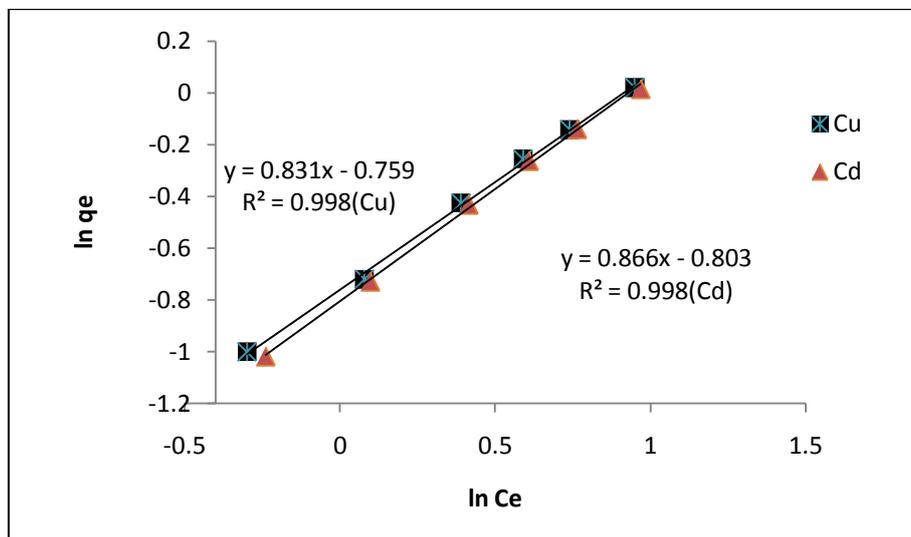
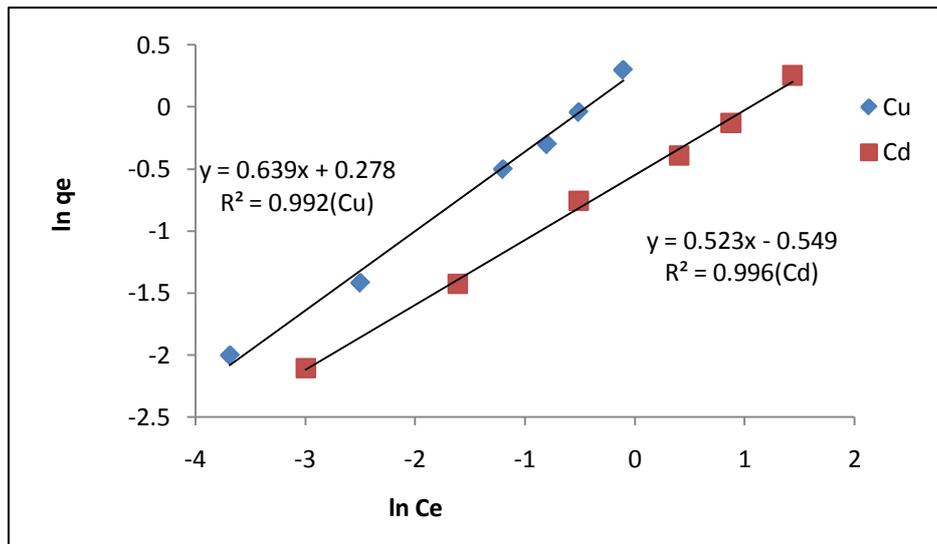


Fig. 13. Freundlich adsorption models for interactions of Cu(II) (II) and Cd on banana peels.



**Fig. 14. Freundlich adsorption models for interactions of Cu(II) and Cd(II) on bentonite**

**Table 3. Langmuir and Freundlich isotherm parameters for Cu (II)**

Adsorbent	Langmuir model				Freundlich model		
	$q_m$ (gm/g)	$K_L$ (l/mg)	$R_L$	$R^2$	n	$K_n$	$R^2$
Banana peels	9.3	0.018050	0.957	0.924	1.21	0.468	0.998
Bentonite	22.8	0.827	0.34	0.928	1.587	1.32	0.9926

**Table 4. Langmuir and Freundlich isotherm parameters for Cd(II)**

Adsorbent	Langmuir model				Freundlich model		
	$q_m$ (mg/g)	$K_L$ (l/mg)	$R_L$	$R^2$	n	$K_n$	$R^2$
Banana peels	8.34	0.0217	0.952	0.912	1.17	0.45	0.998
Bentonite	27.8	1.064	0.278	0.953	1.93	0.577	0.996

### 5.3 Comparison of Metal Ions Removal with Different Adsorbents

A comparison of adsorption capacities ( $q_m$ ) of banana peels and bentonite with some other adsorbents from previous studies are shown in table (5). The values are reported in the form of monolayer adsorption capacity. The results of the present study are higher than some other reported values. Differences in  $q_{max}$  are due to the nature and properties of each

adsorbent such as surface area and the main functional groups in the structure of the adsorbent and the initial concentration. However, the experiments performed to find out the best application of the low-cost adsorbents to treat Cu(II) and Cd(II).

**Table 5: Adsorption capacity of various adsorbents for Cu(II) and Cd(II).**

Adsorbent	Adsorbent capacity(mg/g)		
	Cu(II)	Cd(II)	Reference
Orange peel	3.19	-	12
Sawdust	3.12	-	12
Bagasse	2.89	-	12
Raw date pits	7.4	6.02	25
Activated date pits	33.44	17.24	25
Natural bentonite	30.99	48	29
Acid activated bentonite	36.68	57.88	29
Lemon cortex	-	12	30
Rice husk	10.9		31
Water washed rice husk		8.58	32
Banana peels	9.3	8.34	This study
Bentonite	22.8	27.8	This study

## 6. Conclusion

From the study it can be concluded that:

- 1-The solution pH is an important parameter, which affects the adsorption process. Maximum percentage removal of metals is observed at a pH of 5.0 on both adsorbents.
- 2- The increase of adsorbent dosage had resulted in the increase of percentage removal, the maximum percentage removal was at 2 g.
- 3-The percentage removal increases with decreasing the particle size of the adsorbent material, the maximum removal was at a 75 $\mu$ m particle size.
- 4-The adsorption was decreased with increasing initial metal ions conce. from 2.5 to 30 mg/l.
- 5-Cd(II) was a little bit lower percent removed than Cu(II).
- 6- The adsorption isotherms had fitted Freundlich equation compared with Langmuir equation. However, the adsorption capacity was 9.3 mg/g (Cu<sup>+2</sup>) and 8.34 mg/g (Cd<sup>+2</sup>) on banana peels, and 22.8 mg/g (Cu<sup>+2</sup>) and 27.8 mg/g (Cd<sup>+2</sup>) on bentonite.

7-Bentonite clay manifested a highest adsorption capacity and removal efficiency for Cu(II) and Cd(II) ions higher than banana peels, the present study is conducted to find the technical applicability of the low-cost adsorbents to treat Cu(II) and Cd(II), so, banana peels were used to eliminate heavy metals up to efficiency percentage furthermore it is a low-cost and locally available adsorbent.

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