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Biosorption of Hexavalent Chromium from Aqueous Solution and Tannery Effluent using Banana Peels

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Abstract

Tannery effluent is a major challenge in wastewater management because it contains a lot of chromium (VI); which has deleterious impacts thus remediation treatment is therefore necessary. This study used waste agriculture materials such as banana peels to remove hexavalent chromium. Banana peels were used as adsorbent materials in normal form and nanoparticles. Characterization of normal and nano size of banana peel by transmission electron microscopy (TEM) and FT-IR spectroscopy were evaluated Adsorption experiments were performed on the standard aqueous solutions of Cr (VI) and tannery effluent for varying adsorbent doses; contact times; pH; and concentration of metal. The residual chromium (VI) was determined using the (Inductively Coupled Plasma) ICP. The Langmuir isotherm's model fits the adsorption data perfectly. The nanopowder of banana peels eliminated 98.95% of the residue; compared to the conventional powder of banana peels; which removed up to 72.45%. It has been observed that by using nanometric banana peels; the adsorption efficiency can be increased in a shorter time compared to peels of normal size The isotherm model from Langmuir and the data on adsorption are strongly associated. The results demonstrated that banana peel nanoparticles were effective at chromium adsorption from effluent from tanneries; reaching 95% at 120 minutes; pH 4; and weighing eight grams.

Keywords: Banana peels, Chromium (VI), tannery effluent, adsorption, hydrochloric acid

Introduction

Environmental contamination is a problem; particularly when industrial wastes are found in water sources. Most of the industrial waste is easily transferred into wastewaters; which comprise both organic and inorganic contaminants. Chromium is a naturally occurring metal commonly found in the environment that has two forms: Cr(III) trivalent; and Cr(VI) hexavalent Chromium (VI) has been widely used in industries; such as corrosion protection; textiles; dye manufacturing; leather tanning; electroplating; and fertilizer production that use chromium compounds as raw materials and then release waste into the environment **(Othmani et al.; 2022) (Yasir *et al.*; 2021).** Chromium (VI) is a no biodegradable; toxic and carcinogenic pollutant that can cause nausea; nervous disorder; kidney failure; lung cancer and liver diseases **(Yang *et al.;* 2021; Lou; *et al.;*2021; Fan; *et al.;*2021).** Tanneries effluents are one of the biggest sources of concern in wastewater management because they are laden with heavy metals; especially chromium in the form of chromium (VI) and chromium (III). The chromium sulphate (chrome) employed as the tanning agent is the main source of chromium in tannery effluent. Most small-scale tanning businesses; if not all of them; are unable to afford the pricey traditional wastewater treatment techniques including adsorption; precipitation; and ion exchange. Such techniques fall short of eliminating all hazardous heavy metals from the wastewater. Industries channel untreated or only partially treated effluents containing chromium and other toxic substances as a result **(Ri ;K. *et al.;*2022).** Due to its high surface area; ample resources; diverse surface groups; cost-effective technique; and environmental safety; bioadsorbent; an adsorbent material made from biomass; has attracted significant attention **(Munagapati *et al.;* 2018).** Thus; bioadsorbent is believed to be a capable material for the elimination of heavy metals **(Ali et al.;2016).** The surface groups of the biosorbent for the removal are the main contributor to its high adsorption capacity; where the presence of oxygen; carbon; and mineral fractions causes a chemical adsorption reaction. Banana peel; one of the most popular fruits in the world; makes up between 30 and 40 percent of the weight of the fruit **(Mohammed and Chong2014).** Banana peel (hence referred to as BP) is a common waste that is rich in cellulose and minerals. Large amounts of BP result in significant disposal issues and significant resource waste. It has been established that a variety of functional groups on the BP surfaces; including carboxyl; hydroxyl; and amide groups; are an essential component in the biosorption processes. Additionally; it has carbon at 41.37% **(Mohamedn et al.; 2020).** By repurposing it as sorbent; the disposal of BP can be handled appealingly. Pure and prepared BP had been deployed as a sorbent to extract dissolved heavy metal ions in wastewater owing to its porous structure and variety of surface groups **(Ahmad and Danish 2018).** Chromium that has precipitated into landfills; where it would eventually seep into groundwater during rainy seasons. Heavy metals enter the nearby aquatic bodies. Toxic heavy metals including chromium therefore must be removed from tannery effluent before it is released back into the environment; and this necessitates the development of an affordable; environmentally acceptable technology **(Katenta *et al.;*2020).** The purpose of this study was to extract hexavalent chromium from tannery effluent under various conditions using waste agricultural products; such as banana peels.

Material and method

1. Preparation of sorbent

Banana peels were chosen for this investigation as a natural organic sorbent. The banana peel was purchased at a nearby market. Banana peels were divided into small pieces; cleaned with distilled water; dried in the sun; dried in an oven at 75 °C for 24 hours; and then ground with a regular grinder to produce powder of a normal size while being ground with a nano grinder (Malvern instrument) to produce powder with a nano size. Banana peels of both regular and nanoscale dimensions were characterized using FT-IR and scanning electron microscopy; respectively.

2. Adsorption Studies of chromium from aqueous solution or tannery effluent

Chromium standard solution stock was diluted to the necessary concentrations to create the aqueous solutions (400 and 600 ppm). Additionally; the chromium concentration in tannery wastewater from the leather tanning facility at the point of discharge in the industrial zone of Nasr City; Egypt; was estimated. ICP by The Chrome Tanning Liquor was tested before application with an adsorbent and had a pH of 3.85 and a 1380 mg/L chromium content. Batch adsorption: In the batch tests; banana peels weighing 2.0; 4.0; and 8.0 g were placed in stopper bottles with a capacity of 250 mL and 100 mL of chromium solution. Chromium stock solution was diluted to the required concentrations to create the test solutions. There were 400 and 600 ppm of chromium in the adsorbate. The solutions had pH values of 1.0; 2.0; 3.0; and 4.0. By changing the pH of the solutions using 0.1 N HCl or 0.1 N NaOH solutions; the impact of pH was investigated.PH was measured using a pH meter (Mettler Toledo GmbH; Model: five easy plus FP20Switzerland). The bottles were then periodically shaken by an electric shaker at a constant speed at ambient temperature (25 °C) (30; 60; and 120 min). The differential between the volume of chromium added originally and that remaining after adsorption was used to determine the quantity of chromium adsorbed. The remaining concentrations of chromium in the supernatant were determined using a conductively coupled plasma instrument (HORIBA Scientific; Model: Ultima Expert ICP Optical Emission spectrometer; France); **(Norvell and Lindsay 1978).** The percentage of chromium adsorption by the adsorbents was computed using the equation:

Adsorption % = (C0 - Ce/C0) * 100 (1)

Where; Co and Ce are the initial and equilibrium concentrations of Cr (mg/L) in the solution.

Adsorption capacity was calculated by using the mass balance equation for the adsorbent:

qe= (C0 - Ce) V)/ W (2)

Where; q is the adsorption capacity (mg/g); V is the volume of Cr solution (L) and W is the weight of the adsorbent (g).

Langmuir Equation

Ce/qe=1/a × b+ Ce/a (3)

Where qe=the amount of solute adsorbed per unit weight of adsorbent at equilibrium

b=The Langmuir constant related to the heat of adsorption

a=amount of solute adsorbed per unit weight of adsorbent required for monolayer capacity when Ce/qe is plotted vs. **(Berihun; 2017)**

Results

Characterization of banana peel

Frontier transfer infrared (FT-IR) and transmission electron microscopy (TEM) were used to determine the surface functional groups and partial nature of the banana peel biosorbent. Figure 1a shows how the FT-IR spectra of the normal and nano banana peels displayed comparable spectra; indicating similar chemistry in all samples. In the samples; a signal around 3464 cm^{-1} consistent with the hydroxyl group was found; with the sample exhibiting stronger and wider peaks. Oxygen groups required for metal adsorption are confirmed by the bands at 1635 cm^{-1} and 1411 cm^{-1}; which correspond to C=O and C-O 1049 cm-1 carboxyl groups; respectively. A shift at wave number 586 cm^{-1} was noticed and was assigned to aromatic C-H out of the plane. A band assigned to O=C=O was also found at 2399 cm^{-1}. A band at 2500 cm-1 was due to the thiol S-H stretch. It is generally accepted that the surface area and porous structure affect the physical adsorption of heavy metals on biosorbents with high surface energy and through holes to attract and store ions. The property of BP with a highly porous structure plays an important role in the adsorption process. Furthermore; the TEM image in **Figure 1b**; reveals a nanoparticles nature with a uniform spherical structure. Notably; the average sizes of the spheres were around 30 nm.

Adsorption Studies

Physiochemical factors which affect the magnitude of Cr (VI) adsorption were studied; these factors such as:

1. Equilibrium time 2. Metal ion concentration
3. Adsorbent weight 4. Solution pH

Effect of contact time

Figure (2 and 3) depicts how contact time affects the banana peel's ability to adsorb chromium. Removal ratios grow as time goes on. It is important to note that employing nanometric banana peel particles had a noteworthy effect on removing chromium from the aqueous solution greater than that of using natural banana peels. The maximum percentage of removal of Cr(VI) was done at 120 minutes. The efficiency of nanometric banana peels has reached 1.7 times that of natural banana peels Where the adsorption capacity reached 10.02 mg/g using natural banana peels at a time of 120 minutes; while it reached higher (14.03 mg/g) at a time of 30 minutes using nanometric banana peels. This means that by using nanometric banana peels; the adsorption efficiency can be increased in a shorter time compared to peels of normal size. The additional increase in the reaction time has no significant effect because the available active sites became saturated and reached equilibrium **(Zhou *et al.;* 2017).**

Effect of adsorbent dosage

The impact of adsorbent dose on the banana peel's ability to absorb chromium is shown in Figures (4 and 5). It was observed from the data that the percentage of chromium removal from aqueous solutions increased by increasing the weight of the adsorbent material. The most effective removal of chromium (400 ppm) was done using the largest weight for each of the normal or nanometric peels.

It is worth noting that the maximum removal (73.2%) was reached using the normal peels at a weight of 8.0grams; while the removal percentage reached to 59.1% using the nanometric peels at a weight of 2.0 grams.

Increasing the adsorbent dose resulted in greater adsorption of Cr(VI). The desaturation of the adsorption sites through the adsorption reaction; where the accumulation and overlapping of active sites in blocks above the adsorption leads to a decrease in the effective surface area required for adsorption; is the primary cause of the gradual decline in adsorption efficiency with increasing dose of the adsorbent. This information was consistent with **(Rao *et al.;* 2009)** and **(Routray and Tosh 2012).** which noted that a rise in adsorbent concentration increases the number of active sites that are open to metal ion uptake. Additionally; because the adsorbent has already absorbed the available metal ions; there is no further increase in Cr (VI) adsorption with increased adsorbent mass.

Effect of metal ion concentration

Figure (6) depicts how metal ion concentration affects the amount of chromium that may be absorbed by banana peels.

The results show that when increasing the concentration level of chromium in solution; the percentage of its removal from the aqueous solutions of both normal and nanometer peels were decreased. The average removal percentage reached to41.9 and 65.3% for the concentration of 400 ppm while 39.2% and 56.5% for the concentration of 600 ppm. for both normal and nanometer peels; respectively.

At the ideal concentration (400 mg/L); the ratio of moles of metal ions to the surface area of the adsorbent is high; which prevents interruption of the adsorption process. Higher concentrations cause the adsorbent surface to become saturated; which reduces the amount of time that ions may diffuse from the bulk solution to the adsorbent surface (**Chen *et al.;* 2012**).

Effect of pH

Figure (7;8) demonstrated how pH affected the banana peel's ability to bind chromium. The optimum pH for the maximum uptake of Cr(VI) was found to be pH 4. The removal of hexavalent chromium from the wastewater is highly dependent on the pH of the solution. It is the medium's pH which decides whether the metal is in ionic form and the functional groups attached to it **(Hossain *et al.;* 2012).** At lower pH the adsorbent surface is protonated and there is a strong electrostatic attraction between the positively charged surfaces of the adsorbent with oxyanions of Cr (VI). The interaction between these ions $HCrO^{2-}_4$; $Cr_2O^{2-}_7$ and CrO^{2-}_4 with adsorbent surface decreases at higher pH; as at higher pH the surface of adsorbent becomes negatively charged and there is an abundance of hydroxyl ions in aqueous solution **(Gupta and Rastogi; 2009).**; the optimum pH; however; was observed between pH 1;2;3 and 4.

Generally; the porous banana peel precursor was found to be an effective bioadsorbent for the removal of Cr (VI) from an aqueous solution. Banana peel biomass containing a variety of chemical groups such as carboxylic acid and hydroxyl groups which act as active centers for the adsorption of metal ions from aqueous media and industrial wastewater. The presence of these functional groups were shown in the FTIR spectra; these results are consistent with what was mentioned **(Mohamed *et al.;*2020).** Essentially; the sorbent produced in this study could be a promising; environmentally friendly; and low-cost bio filter for the remediation of Cr(VI) from aqueous environments to protect public health **(Kabir *et al.;*2022).**

Langmuir isotherm model

Langmuir adsorption models were used to study the interaction of Cr (VI) with adsorbent (**Figure 9;10**). The adsorption data are in close agreement with the Langmuir isotherm model. The R^2 values are less than one which shows that the adsorption data are fully fitted with the Langmuir isotherm model and the adsorption of Cr (VI) onto banana peel is favorable. The literature study shows that the Langmuir model is more suitable for describing the adsorption isotherm of Cr (VI) onto various adsorbents **(Gholipour. et al.;2011; Choia; *et al.;* 2009).**

Removal % of chromium from tannery wastewater using normal and nano-size of banana peel

Tanneries water; in which chromium was estimated (1380 mg/l) was used to evaluate the efficiency of using banana peels in the form of normal and nanometric size under the influence of the optimal conditions obtained from this study (pH; Cr concentration; contact time and adsorbent weight). The obtained results showed that banana peels; whether of normal or nano size; had a superior ability to absorb chromium; so the adsorption efficiency reached 81.06 and 97.95 % for both normal and nanometric peels; respectively (**Figure 11**). This study is consistent with the case study of removing chromium from tannery effluent by a low-cost sorbent (**Nur-E-Alam; *et al.;*2020**).

Conclusion

Banana peel nanoparticles act as good adsorbents for Cr(VI) removal, and it was observed that the use of nano banana peels can improve the adsorption efficiency in a shorter time compared to normal-sized peels. The optimum pH of Cr(VI) was determined to be 4.0; the amount of adsorbent was 8 g/L; the concentration was 400 mg/L; and the contact time was 120 min. Tanning water containing hexagonal chromium can be treated in a natural; environmentally friendly; and cost-effective way.

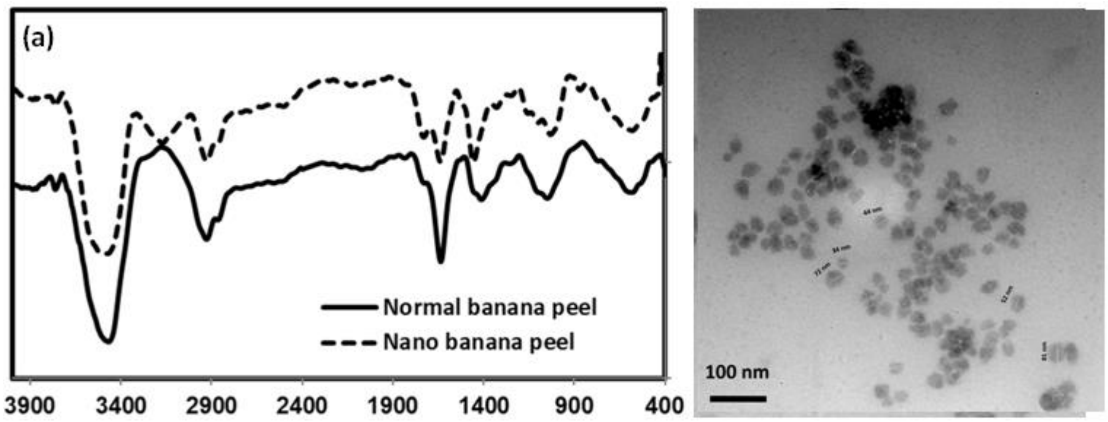
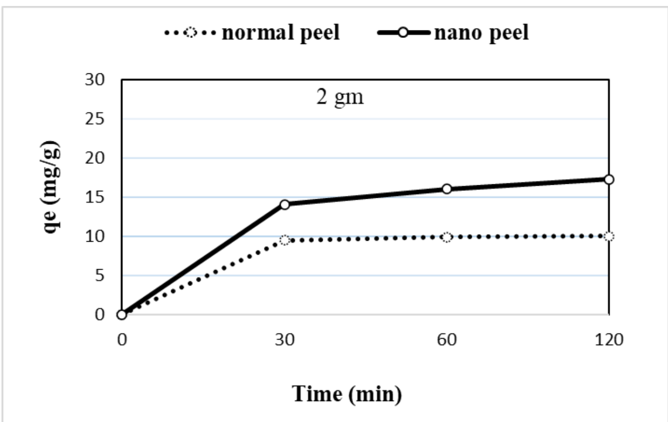


Figure 1. a) FT-IR spectra and (b) HR-TEM images of the banana peel



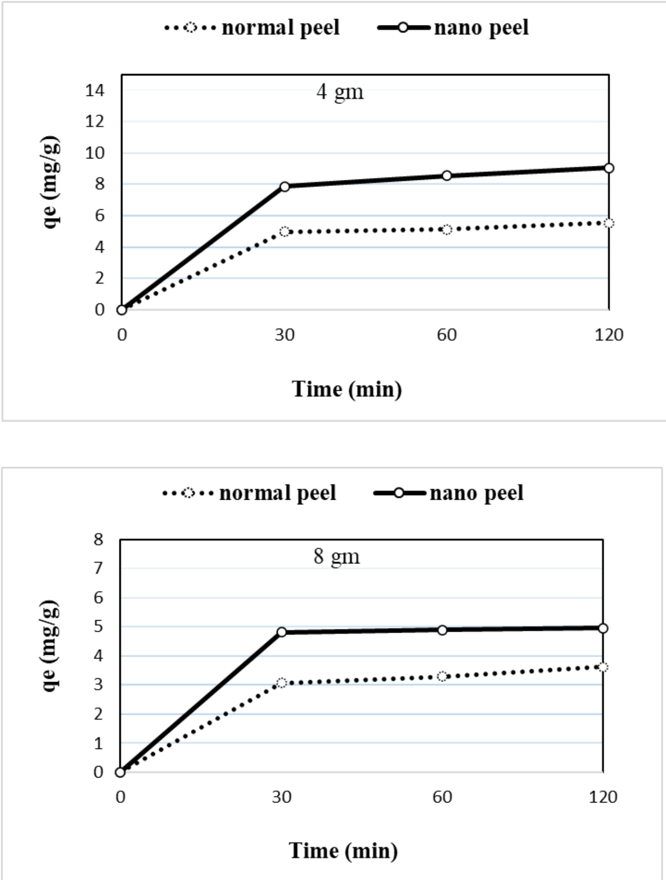
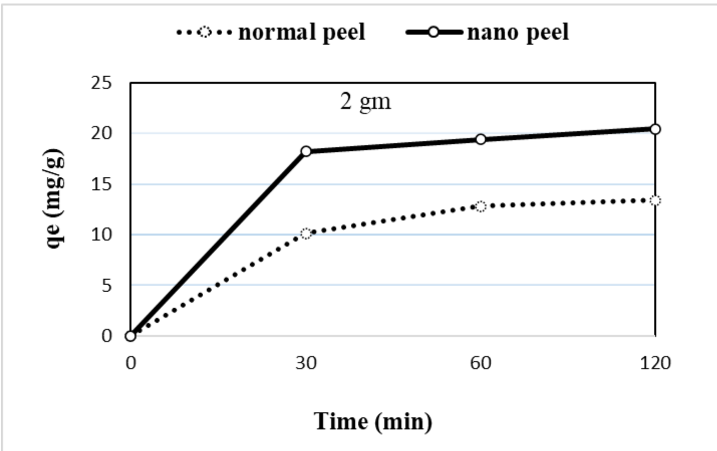


Fig. (2): Effect of time contact on Cr removal from aqueous solution by different weights of banana peel (conc. of Cr= 400 ppm; pH=4; Temp.= 25 °C)



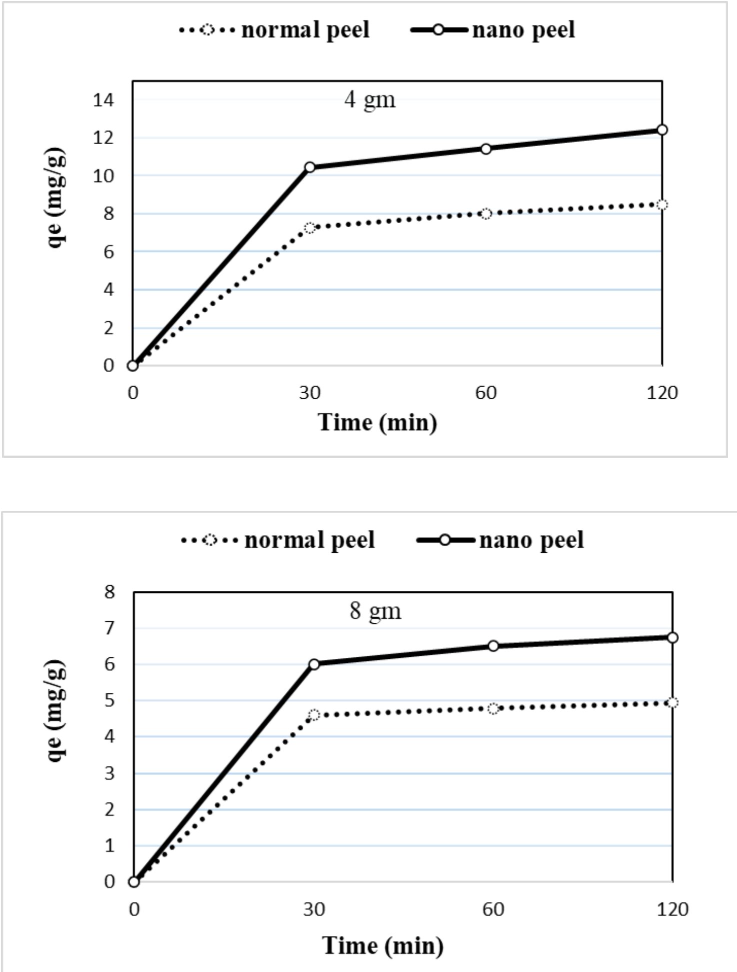


Fig. (3): Effect of time contact on Cr removal from aqueous solution by different weights of banana peel (conc. of Cr= 600 ppm; pH=4; Temp.= 25 °C)

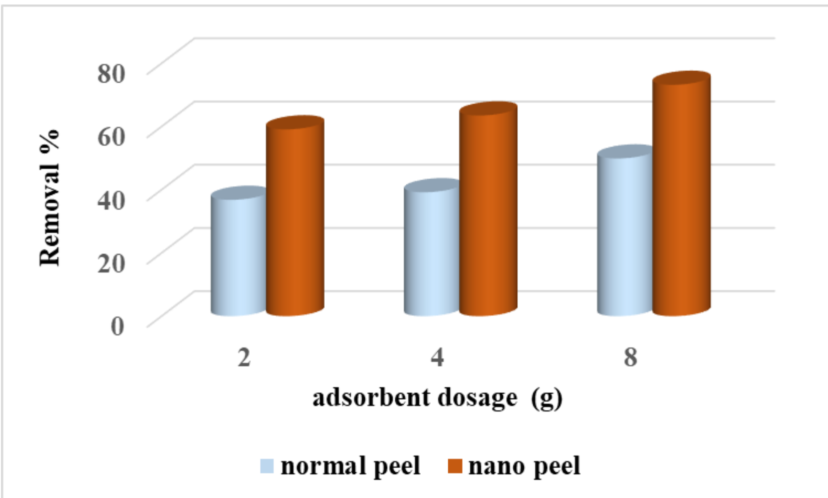


Fig. (4): Effect of adsorbent dosage on Cr removal from aqueous solution using banana peel (conc. of Cr= 400 ppm; pH=4; Temp.= 25 °C)

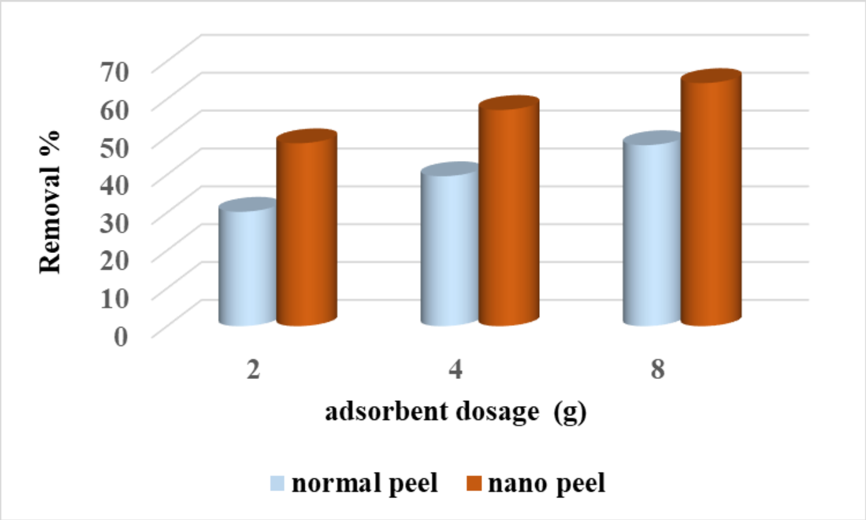


Fig. (5): Effect of adsorbent dosage on Cr removal from aqueous solution using banana peel (conc. of Cr= 600 ppm; pH=4; Temp.= 25 °C)

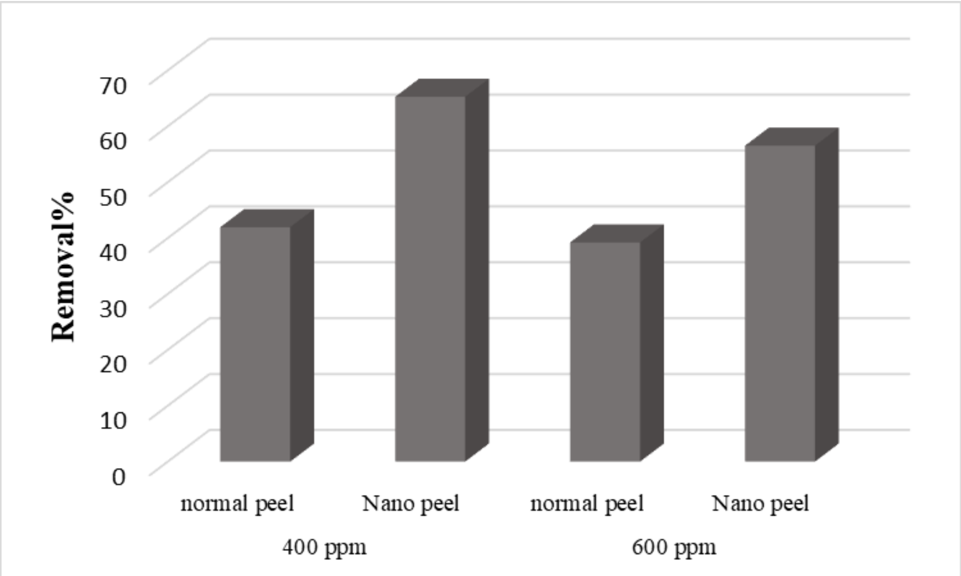


Fig. (6): Effect of concentration of metal on removal% from aqueous solution by using banana peel

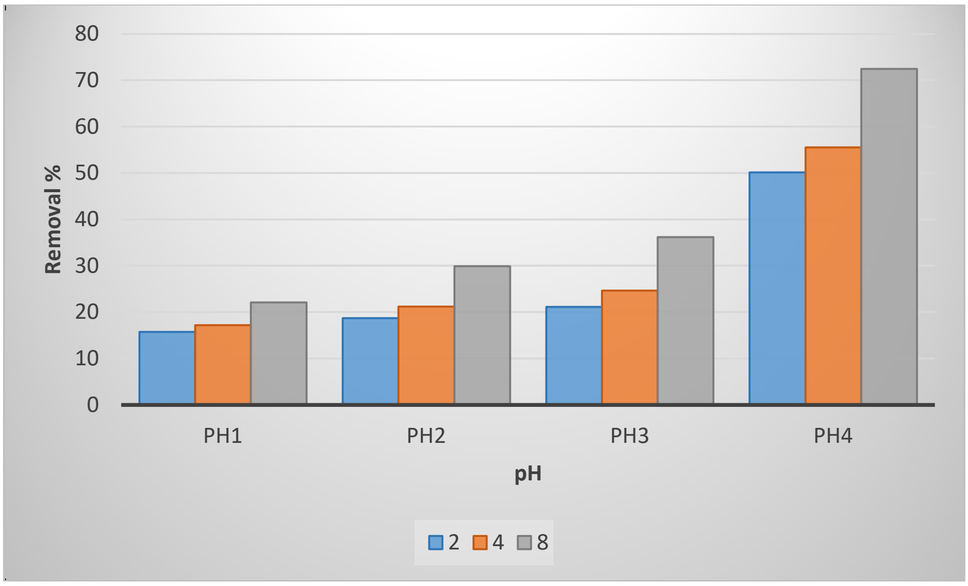


Fig. (7): Effect of pH on removal% from aqueous solution by using banana peel Normal

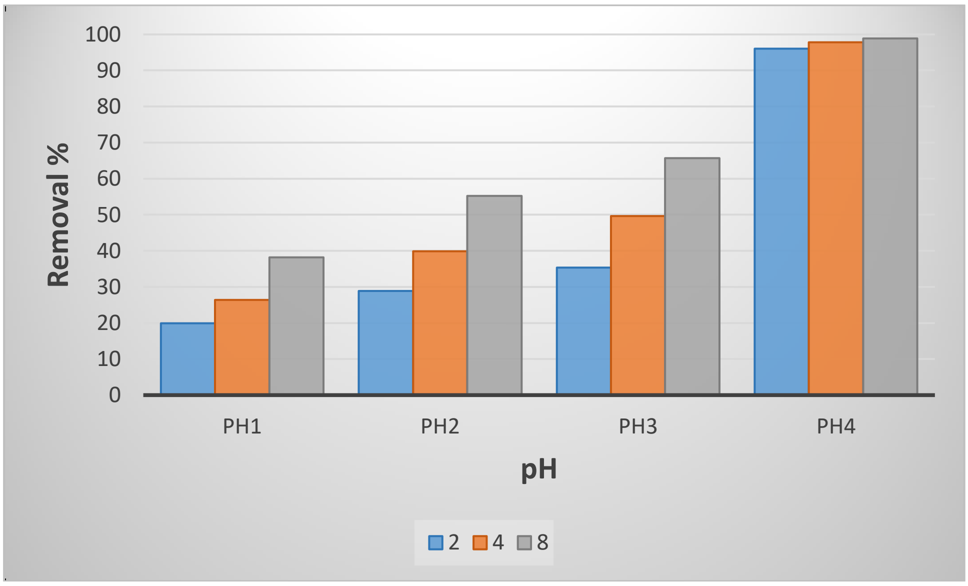
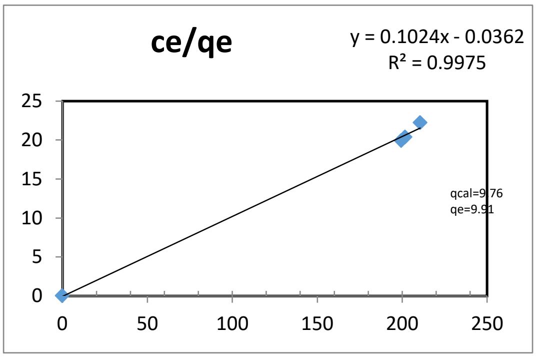
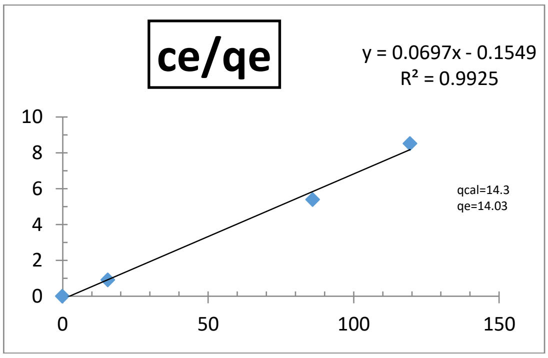


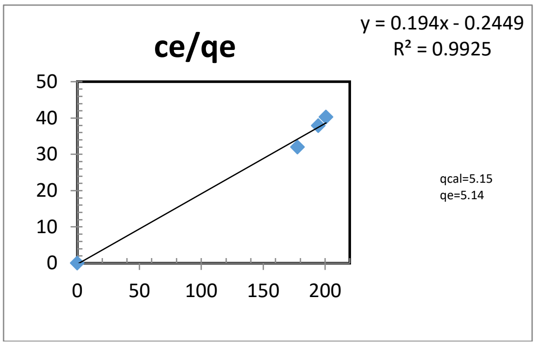
Fig. (8): Effect of pH on removal% from aqueous solution by using banana peel Nano



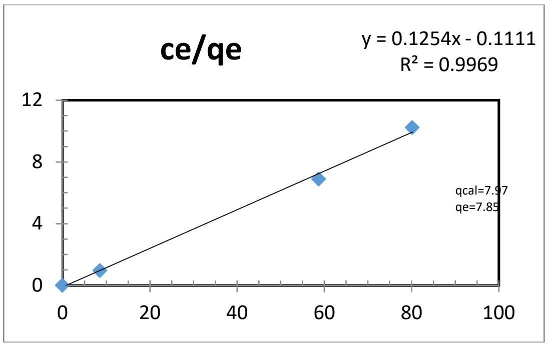
Normal peel; 2g; 400ppm



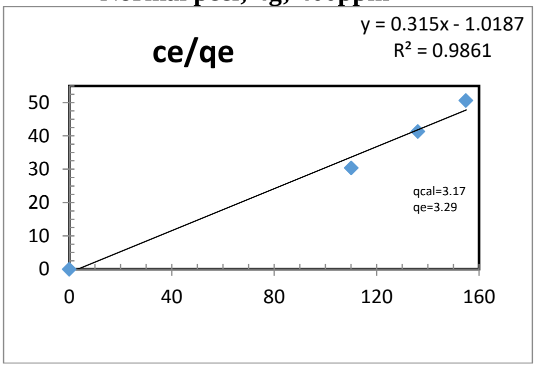
Nano peel; 2g; 400ppm

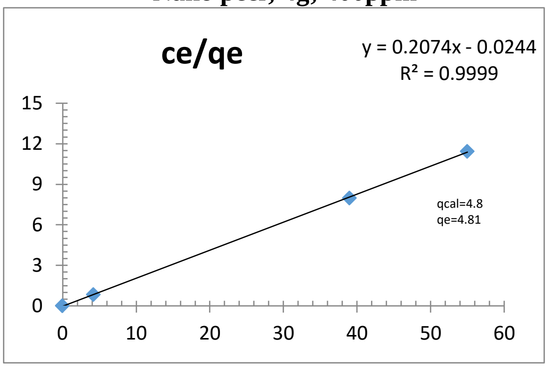


Normal peel; 4g; 400ppm



Nano peel; 4g; 400ppm

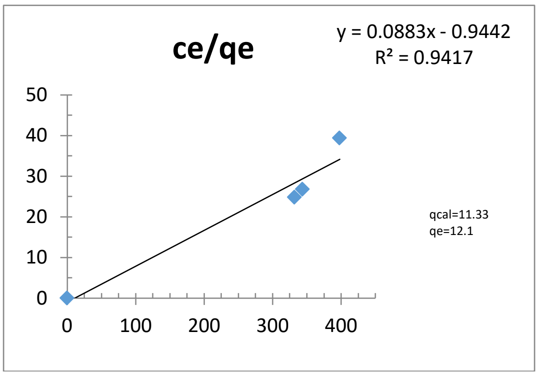




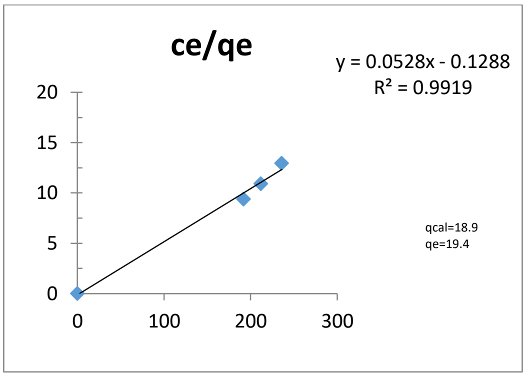
Normal peel; 8g; 400ppm

Nano peel; 8g; 400ppm

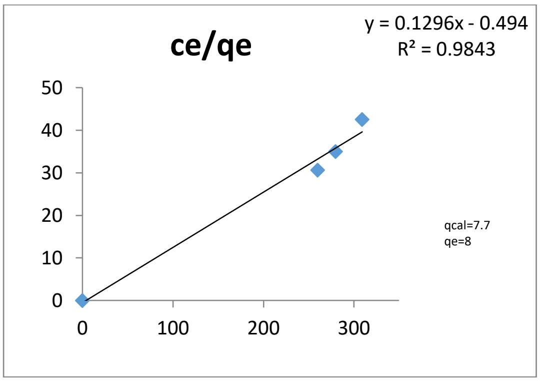
Figure 9. Langmuir adsorption isotherm model for Cr(VI) 400 ppm onto banana peel



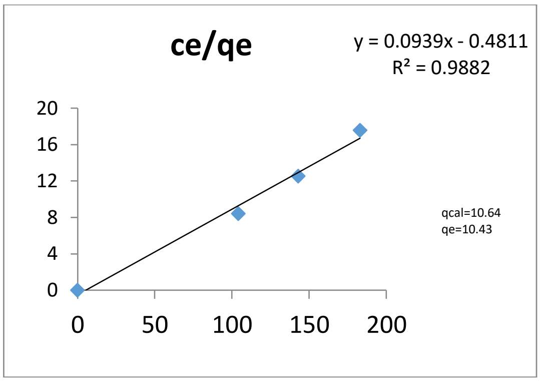
Normal peel; 2g; 600ppm



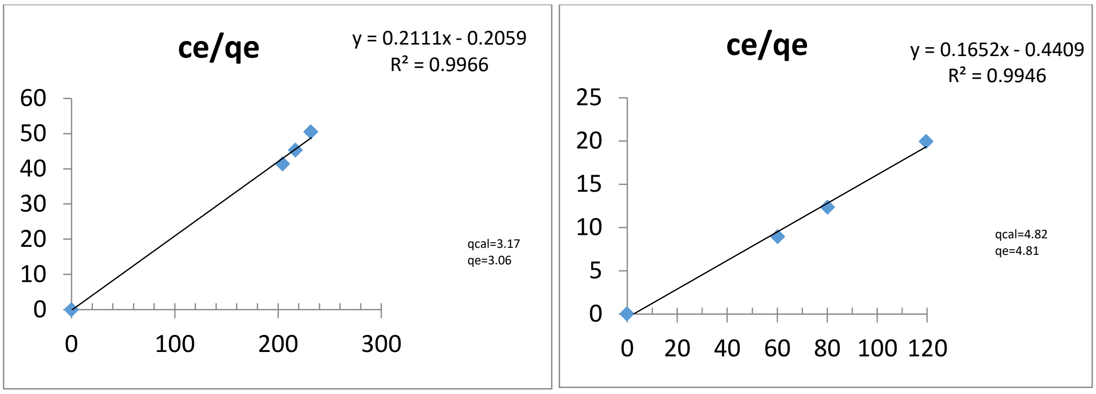
Nano peel; 2g; 600ppm



Normal peel; 4g; 600ppm



Nano peel; 4g; 600ppm



Normal peel; 8g; 600ppm **Nano peel; 8 g; 600ppm**

Figure 10. Langmuir adsorption isotherm model for Cr(VI) 600 ppm onto banana peel.

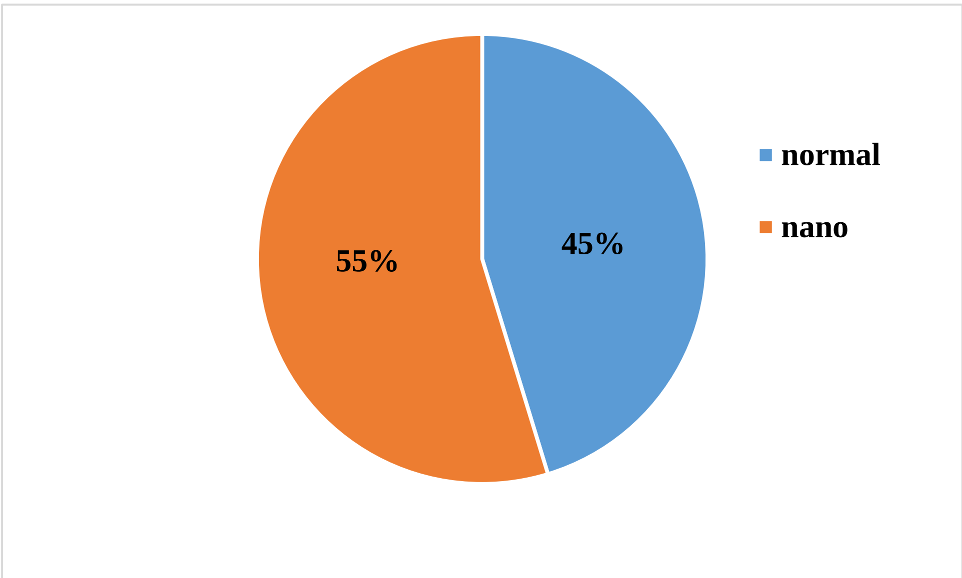


Figure 11: Removal % of chromium from tannery wastewater using normal and nano-size of banana peel

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الامتصاص الحيوي للكروم السداسي التكافؤ من المحاليل المائية ومياه صرف المدابغ باستخدام قشور الموز

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تمثل مياه المدابغ السائلة تحديًا كبيرًا في معالجة مياه الصرف الصحي لاحتوائها على تركيزات عالية من الكروم السداسي؛ والتي لها آثار ضارة في مياه الصرف وبالتالي فإن العلاج لها ضروري. استخدمت هذه الدراسة مخلفات المواد الزراعية مثل قشور الموز لإزالة الكروم سداسي التكافؤ. تم استخدام قشور الموز كمواد ممتزة في صورتها الطبيعية والجسيمات النانوية. تم تقييم توصيف الحجم الطبيعي والنانو لقشر الموز بواسطة المجهر الإلكتروني النافذ (TEM) ومطيافية FT-IR. وأجريت تجارب الامتزاز على المحاليل المائية القياسية للكروم السداسي ومياه صرف المدابغ بجرعات ماصة مختلفة؛ أوقات الاتصال؛ درجة الحموضة. وتركيز المعادن. تم تقدير تركيز الكروم السداسي المتبقي باستخدام جهاز الانبعاث الذرى باستخدام البلازما المستحثة . يتناسب نموذج لانجمير متساوي الحرارة مع بيانات الامتزاز بشكل مثالي. مسحوق النانو من قشور الموز يزيل 98.95% من الكروم السداسي مقارنة بمسحوق قشور الموز التقليدي؛ والتي أزالت ما يصل إلى 72.45٪. وقد لوحظ أنه من خلال استخدام قشور الموز النانومترية؛ ويمكن زيادة كفاءة الامتزاز0 في وقت أقصر مقارنة بالقشور ذات الحجم الطبيعي. ويرتبط نموذج لانجمير والبيانات الخاصة بالامتزاز بقوة. أظهرت النتائج أن الجسيمات النانوية لقشر الموز كانت فعالة في امتصاص الكروم السداسي من النفايات السائلة الناتجة عن المدابغ تصل إلى 95%خلال فترة زمنية 120 دقيقة والرقم الهيدروجيني = 4 ووزن مادة الادمصاص ثماني جرامات.