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Hexavalent Chromium Adsorption by Watermelon Peels From Tannery Wastewater

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In Loving Memory of Late Professor Doctor ""Mohamed Refaat Hussein Mahran""

Abstract

The leather tanning industry is releasing Chrome Hexavalent Cr(VI), resulting in detrimental consequences and requiring remedial intervention. This study investigated the possible application of watermelon peels as a bio-adsorbent for removing Cr(VI) from water-based solutions, using watermelon peels in their normal state and watermelon peel nanoparticles. Transmission electron microscopy (TEM) and FT-IR spectroscopy were used to characterize watermelon peels. The tannery wastewater and standard Cr(VI) water solutions were used in adsorption tests with a range of adsorbent amounts, contact times, pH 4, and temperatures (25 °C). The residual Cr(VI) was determined using inductively coupled plasma (ICP). The Langmuir isotherm's model fits the adsorption data perfectly. Results showed that the watermelon peels of normal powder and nanopowder were removed up to 77.61% and 100%, respectively, at an aqueous solution of 400 ppm of Cr(VI), pH 4, the amount of adsorbent was 8 gram/liter, the temperature was 25 °C, and the contact time was 120 minutes. Additionally, the watermelon peels of normal powder and nanopowder were removed up to 62.31 and 74.45%, respectively, at an aqueous solution of 600 ppm of Cr(VI), pH 4, the amount of adsorbent was 8 gram/liter, the temperature was 25 °C, and the contact time was 120 minutes. Therefore, we recommend using nano watermelon peels since they improve adsorbing Cr(VI) efficiency in a shorter period compared to regular-sized peels. Furthermore, the isotherm model from Langmuir and the data on adsorption are strongly associated.

Keywords: Adsorption; Cr(VI); tannery effluent; watermelon peels

1. Introduction

The ability to produce leather with qualities required for high-quality leather, such as good hydrothermal stability, improved dyeing properties, and suppleness, has made chrome tanning the most popular technology in the leather industry globally [10]. However, the method has drawn criticism worldwide for seriously harming the environment and negatively affecting human health and other living things [15].

For people, plants, and other living things, an increasing amount of dangerous trace metals (loids) presents a significant risk to their survival in the environment [24]. The contamination of food caused by the release of hazardous trace elements into the water, which is increasing water pollution, poses a severe threat to the food chain [6], [27]). Additionally, the worldwide demand for water resources is significantly increased by the presence of these heavy metals (loids) in water streams [20].

With a ranking among the top sixteen most hazardous chemicals, chromium is extremely dangerous. Its teratogenic and carcinogenic properties have become a significant health concern [4]. While the majority of Chrome Hexavalent Cr (VI) compounds are poisonous and can have carcinogenic effects, Chrome Trivalent Cr(III) is necessary for human nutrition, especially in the metabolism of glucose [18].

Water contaminated with Cr(III), especially Cr(VI), is a severe problem for humans and the environment because of its toxicity and potential to cause sickness. Also, Cr(III) can be found in the earth's crust as ores and in several complex forms [33]. The dumping of industrial effluents from the ceramics, electroplating, pigment, dye, and metal finishing sectors is one of the sources of Cr(III) pollution in water bodies, as the majority of the valence states of chromium metal, which range from 2 to +6, are found at pH<6 [12].

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There are two stable oxidation states of Cr(III) in the natural world Cr(III) and Cr(VI) [1]. Cr(III) is slightly harmful and can be used by the body as a micronutrient [22]. Comparatively more water-soluble than Cr(III), Cr(VI) is a very mobile, toxic, and stable species (Cr(III)) [15]. Because Cr(VI) is 500 times more hazardous than Cr(III), it has been designated as a Class-I human carcinogen [2], [21].

Precipitation, extraction of solvents, buoyancy, osmosis (reverse), and ion exchange are some of the processes that have been established to be used with Cr(VI) originating from wastewater [16]. However, these traditional systems' increased capital costs and energy requirements have shown them to be both expensive and unworkable [21]. Adsorption has recently become a popular and affordable technique for removing Cr(VI) from contaminated water [19]. Bioadsorbent, a material derived from biomass, has gotten much attention because it has a lot of surface area, many resources, different types of surface groups, tiny volume pores, good physicochemical properties, resistance to the generation of hazardous substances during adsorption, and is safe for the environment [34]. The capacity of a wide range of waste adsorbents, such as agricultural wastes, including coffee waste, jatropha waste, peels of citrus fruits, watermelon peels, coconut fiber, wheat stalks, and other heavy metals such as lead from polluted water, has been investigated in the past [21].

The fruit known scientifically as the watermelon (Citrullus lanatus) is one of the most popular in the world, and it is also among the most affordable and widely available fruits in Egypt, though it is now available all year in Egypt because of its tropical nature, the output is often highest in the summer [9]. The fruit's rind makes up around 30% of its overall weight, compared to the fruit's edible meat, which makes up about 70% of the fruit [30]. The watermelon peel, which is typically discarded in large quantities, is made up of carbonaceous substances like polysaccharides like cellulose, pectin, and other such substances, carotenoids, and low molecular weight substances like citrulline and other amino acids, as well as other phytochemical compounds. Also, it has several characteristics that make it a suitable medium for synthesizing activated carbon compounds, which serve as very efficient adsorbents for heavy metals [9].

In recent times, there has been a growing use of nano-adsorbents in wastewater treatment. This is because they have a small size, a larger surface area, and improved chemical activity. These factors affect their ability to adsorb substances and their physical, chemical, and material properties [3].

The present study aimed to investigate the effectiveness of low-cost and environmentally friendly materials such as agricultural waste watermelon peels for the removal of Cr(VI) from liquid tanning water. Additionally, we assessed the effect of different conditions, such as contact time, dosage of adsorbents, and concentration of chromium on the removal capacity. Furthermore, we aimed to evaluate the effectiveness of nanoforms of these wastes for the same purposes and determine the best treatment to remove Cr(VI) from the wastewater of chrome tanning.

2. MATERIALS AND METHODS

In this study, watermelon peels were selected as a natural organic sorbent. Watermelon peels were obtained from waste fruit juice from the Food Technology Research Institute in the Agriculture Research Center (ARC). Tanneries water was obtained from Hussein Al-Jabbas Egyptian leather factory; in the Al Rubiki area, the Cr(III) concentration was estimated.

All reagents and chemicals of analytical reagent grade were obtained from Sigma-Aldrich. The solutions were prepared in double distilled water. The standard solution used in this study was potassium dichromate (K2Cr2O7). The Cr (VI) stock solution, with a concentration of 1000 mg/L, was created by dissolving 2.829 g of analytical-grade potassium dichromate, K2Cr2O7, in 1000 mL of deionized water. The initial stock solution was diluted with distilled water to achieve the target concentration range of the test solution (400 ppm–600 ppm).

The watermelon peels were diced, rinsed with distilled water, sun-dried, oven-dried at 75ºC for 24 hours, and pulverized into a powder [38]. The peels were pulverized into tiny fragments using a standard grinder model JML from China for the regular-size powder. The normal powder peels were mixed with the nano grinder AllWin, model HZPlus30, also from China, and processed into a fine powder for the nanopowder. This information is based on the studies conducted by [3], [7].

The samples were examined for structure and particle size distribution by Transmission Electron Microscopy (TEM) [17].

Fourier transform infrared spectroscopy (FT-IR) was performed to study and obtain the surface functional group in BP and WMP (normal-size powder and nanopowder). The measurement range for the examined samples was 450–4000 cm–1. The sample was carried out (FT-IR) in Central Laboratory, Faculty of Agriculture, Cairo University in Faculty of Agriculture –Cairo University- model Nicolet TM iS10.

The batch experiments were conducted using three weights (2.0, 4.0, and 8.0 g) of watermelon peels in 250 mL capacity stopper bottles with 100 mL of Cr(VI) solution. The test solutions were prepared by diluting a stock solution of Cr(VI) to the desired concentrations. The adsorbate concentration Cr(VI) was 400 and 600 mgL1. The bottles were then shaken at a uniform speed of 200 rpm at room temperature (25.5 °C) by using an electric shaker Bio Base model Sk-0180- Pro (China) for time intervals (30, 60, and 120 min). The difference between the quantity of Cr(VI) added initially and the amount that remained after adsorption was used to calculate the quantity of Cr(VI) adsorbed. The remaining concentrations of Cr(VI) in the supernatant were analyzed for the metal using Inductively Coupled Plasma (ICP) OPTICAL EMISSION SPECTROMETER HORIBA Scientific. The adsorbents' %Cr(VI) adsorption was calculated according to [5], and the Langmuir Equation was calculated according to [8].

Statistical analysis

All of the analyses were performed in three independent replications for each sample. All the experimental data are expressed as mean ± SD. ANOVA was analyzed using SPSS 20.0 software. Duncan's multivariate range test determined the mean difference, and $p < 0.05$ indicated statistical significance. Origin 2018 software was used for charting.

3. RESULTS AND DISCUSSION

3.1. Characterization of watermelon peels

Frontier transfer infrared FT-IR spectroscopy is the most advanced method for analyzing and identifying functional groups in natural materials and manufactured compounds. The FTIR spectrometer was utilized to identify the functional groups on the surface of the watermelon peels. Generally, FTIR spectra revealed the presence of amines, alcohol, carboxylic acid, hydroxyl groups, phenol, alkanes, amino acids, alkyl halide, and aromatic compounds in the watermelon peels. An intense band with high absorbance has been detected at around 3403 cm^{-1}, perhaps indicating the presence of -NH or -OH functional groups. This band has increased depth, indicating a higher absorption level, as illustrated in **Figure 1 [7, 13]**.

The prominent and intense peak at 3403.5 cm^{-1} indicates the stretching vibrations of AOH groups in cellulose, pectin, and lignin. Additionally, the peaks seen at 2928.33 cm-1 in the normal peel are attributed to the stretching vibrations of ACH groups in methyl and methoxy groups, while in nano size reached 2928.23 cm^{-1} A peak at 2135.77, 2150.39 cm-1 (normal and nano) corresponds to the AC,O stretching of carboxylic acid or esters, as well as the asymmetric and symmetric vibrations of ionic carboxylic groups (ACOOA). The normal form had a band at 1620.15 cm^{-1}, while the nano form had a band at 1621.80 cm^{-1}. Similarly, the normal and nano forms had peaks at 1419.16 cm-1 and 1418.7 cm-1, respectively. The band at 1248.16,1251.43 cm-1 can be attributed to the symmetric stretching of ACOOA in pectin. The peaks observed between 1300 and 1000 cm^{-1} can be attributed to the stretching vibrations of carboxylic acids and alcohol **[28].**

As illustrated in **Figure 2**, scanning electron microscopy was utilized to determine the surface texture and morphological characteristics of the watermelon peels. Upon initial observation, HR-TEM graphs of watermelon peels reveal the presence of holes with irregular shapes. However, these pores appear to be evenly spread throughout the whole surface and possess a smooth texture. Watermelon peels possesses a high binding capacity because to the existence of pores with uneven shapes **[25].**

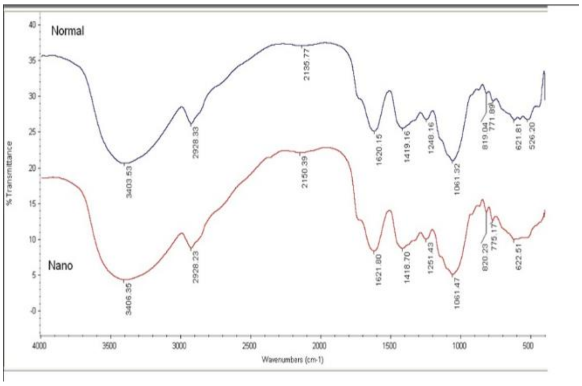


Figure (1): FT-IR spectra for watermelon peel normal and nano peel.

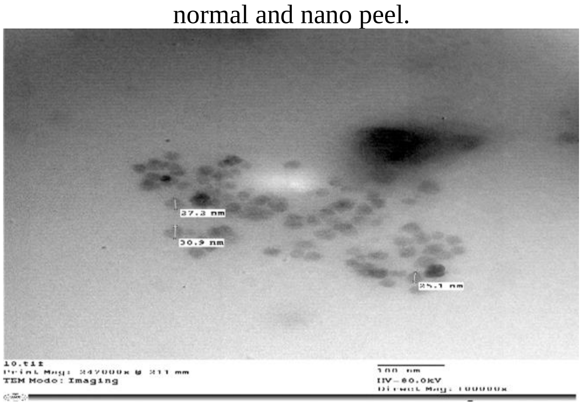


Figure 2: HR-TEM images of the nano watermelon peel.

3.2. Adsorption studies

These tests employed the following methodology to examine the variables influencing the effectiveness of the Cr(VI) adsorption process from contaminated solutions:

3.2.1 Effect of Contact Time

The time of contact between the solution of dye and sorbent has been revealed as a highly valuable parameter in sorption investigations. The effect of contact time on the adsorption of Cr(VI) by watermelon peel was shown in tables (1 and 2) and figures (3 and 4). Removal ratios increase significantly ($p < 0.05$) with the increment in time. The maximum % removal of Cr(VI) has done at 120 min. It was found that there was a noticeable effect on removing Cr(VI) from the aqueous solution using nano-metric particles of watermelon peels greater than that of natural watermelon peels. The efficiency of nano-metric watermelon peels reached 1.5 times that of natural ones. The adsorption capacity reached 67.30 and 77.61% using natural watermelon peels at 60 and 120 minutes, respectively. While the capacity reached 83.22 and 100% at 60 and 120 minutes, respectively, using nano-metric watermelon peels. This means that by using nano-metric watermelon peels, adsorption efficiency can be increased in a shorter time than normal-sized peels. The additional increment in the reaction time had no significant effect because the active sites that were accessible got fully saturated and achieved a state of equilibrium **[14]**.

Table (1): The impact of contact time on the elimination of Cr(VI) (400 ppm) from aqueous solutions using varying quantities of watermelon peels.

effect of contact time (2g) 400 ppm Cr(VI)				
	raw peel		nano peel	
Time	%removal	qe	%removal	qe
0	0	0	0	0
30min	23.50 ± 1.21^{c}	4.70 ± 0.35^{c}	32.65 ± 1.56^{c}	6.53 ± 0.73^{c}
60min	26.0 ± 1.21^{b}	5.2 ± 0.35^{b}	49 ± 1.56^{b}	9.8 ± 0.73^{b}
120min	37.5 ± 1.21^{a}	7.2 ± 0.35^{a}	51.2 ± 1.56^{a}	10.24 ± 0.73^{a}
effect of contact time (4g) 400ppm Cr(VI)				
	raw peel		nano peel	
Time	%removal	qe	%removal	qe
0	0	0	0	0
30min	32.8 ± 1.68^{c}	3.28 ± 0.12^{c}	59 ± 2.05^{c}	5.90 ± 0.42^{c}
60min	46 ± 1.68^{b}	4.6 ± 0.12^{b}	74.11 ± 2.05^{b}	7.41 ± 0.42^{b}
120min	55.5 ± 1.68^{a}	5.55 ± 0.12^{a}	83.41 ± 2.05^{a}	8.34 ± 0.42^{a}
effect of contact time (8g) 400ppm Cr(VI)				
	raw peel		nano peel	
Time	%removal	qe	%removal	qe
0	0	0	0	0
30min	41.45 ± 2.18^{c}	2.07 ± 0.09^{c}	64.45 ± 3.05^{c}	3.22 ± 0.14^{c}
60min	67.30 ± 2.18^{b}	3.36 ± 0.09^{b}	83.22 ± 3.05^{b}	4.16 ± 0.14^{b}
120min	77.61 ± 2.18^{a}	3.88 ± 0.09^{a}	100 ± 3.05^{a}	5.0 ± 0.14^{a}

a, b & c: There is no significant difference ($P > 0.05$) between any two means, within the same column with the same superscript letter.

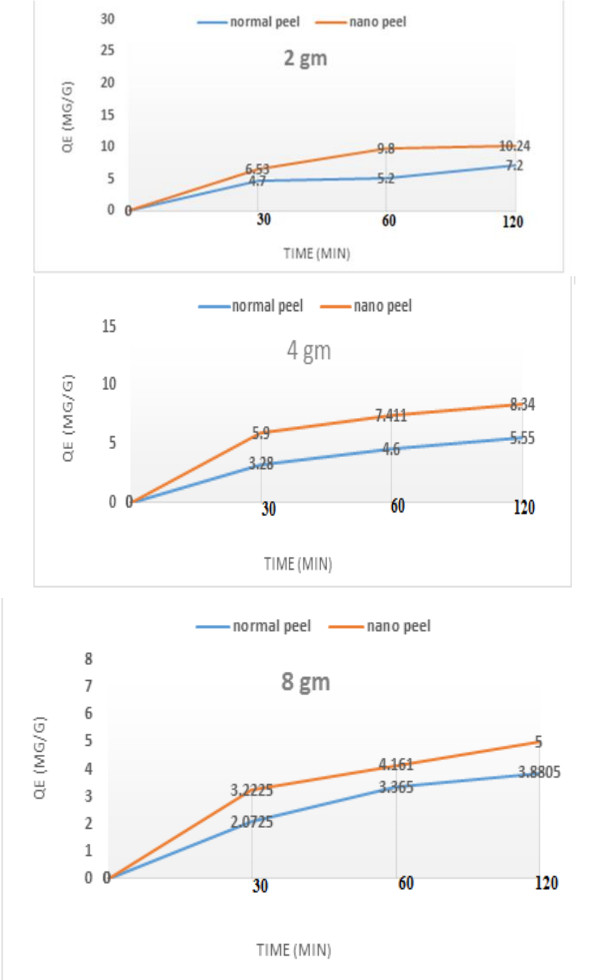


Figure (3): The impact of contact time on the elimination of Cr(VI) (400 ppm) from aqueous solutions using varying quantities of watermelon peels.

Jain *et al.* [36] found that neem leaf powder, when used as an adsorbent, removed Cr(VI) from water-based solutions at an 85% rate when the contact time between the adsorbent and solution was increased. Compared to the results of this experiment, it is lower.

3.2.2. Influence of adsorbent dosage:

The dose of adsorbent is a crucial element investigated during batch mode investigations.

The impact of adsorbent dosage on the elimination of Cr(VI) was investigated by agitating 100 mL of a solution containing initial concentrations of Cr(VI) ions (2, 4, and 8g) with melon peel. The study revealed a strong correlation between the adsorbent concentration and the adsorption, as shown in Figures (5 and 6). Furthermore, the adsorption increased proportionally with higher dosages of the adsorbent.

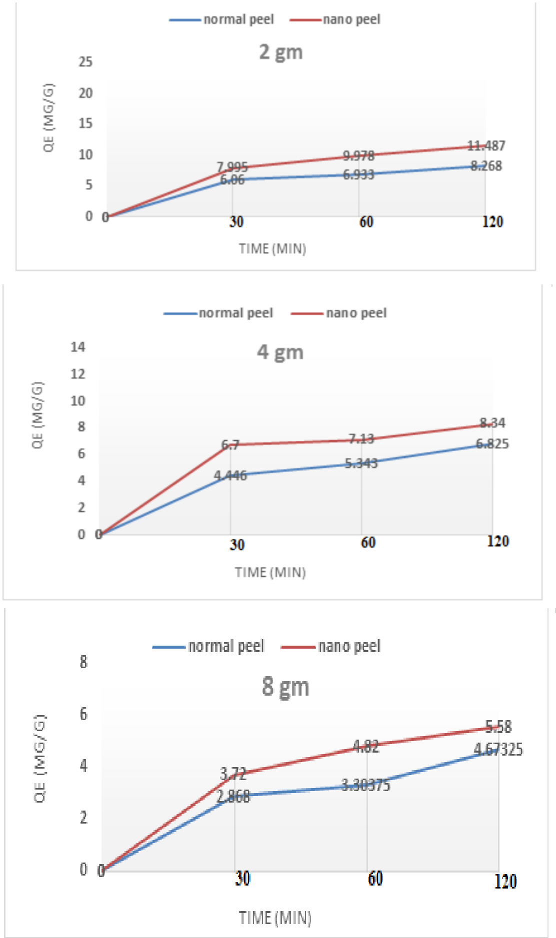


Figure (4): The impact of contact time on the elimination of Cr(VI) (600 ppm) from an aqueous solution using varying amounts of watermelon peels

The most significant removal achieved with conventional peels equaled 77.61%, but the maximum removal achieved with nano-metric peels Cr(VI), equaled 100% at 8.0 grams and 400 ppm Cr(VI). At a weight of 8.0 grams and 600 ppm, regular peels may be removed up to 62.31% of the maximum amount of Cr(VI), but nano metric peels removed up to 74.45 percent of the maximum amount of Cr(VI) at the same weight.

Cr(VI) elimination increased as the adsorbent's dosage was raised. However, the desaturation of the adsorption sites through the adsorption reaction, where the accumulation and overlapping of active sites in blocks above the adsorption led to a decrease in the effective surface area required for adsorption, was the main cause of the gradual decrement in adsorption capacity with increasing dose of the adsorbent. This information was consistent with that provided by **[26]**.

It has been shown that a higher amount of adsorbent leads to an increase in the quantity of active sites that may absorb metal ions **[32]**.

Increasing the dosage further led to a reduction in l oading ability, but elimination efficiency remained th e same. One possible explanation for why adsorption increases with adsorbent dose is that there are more surface active sites available; another possible explanation for why efficiency decreases with increasing adsorbent concentration is that there are fewer surface active sites as a result of partial grouping of the adsorbent **[28].**

Table (2): Impact of contact time on the elimination of Cr(VI) (600 ppm) from an aqueous solution using varying quantities of watermelon peels.

effect of contact time (2g) 600ppm Cr(VI)				
	raw peel		nano peel	
Time	%removal	qe	%removal	qe
0	0	0	0	0
30min	20.2± 1.34^{c}	6.06± 0.24^{b}	26.65± 2.09^{c}	7.99± 0.31^{c}
60min	23.11± 1.34^{b}	6.93± 0.24^{b}	33.26± 2.09^{b}	9.98± 0.31^{b}
120min	27.56± 1.34^{a}	8.27± 0.24^{a}	38.29± 2.09^{a}	11.49± 0.31^{a}
effect of contact time (4g) 600ppm Cr(VI)				
	raw peel		nano peel	
Time	%removal	Qe	%removal	qe
0	0	0	0	0
30min	29.64± 2.26^{c}	4.45± 0.21^{c}	44.65± 3.01^{c}	6.69± 0.24^{c}
60min	35.62± 2.26^{b}	5.34± 0.21^{b}	47.53± 3.01^{b}	7.13± 0.24^{b}
120min	45.50± 2.26^{a}	6.83± 0.21^{a}	55.57± 3.01^{a}	8.34± 0.24^{a}
effect of contact time (8g) 600ppm Cr(VI)				
	raw peel		nano peel	
Time	%removal	Qe	%removal	qe
0	0	0	0	0
30min	38.24± 3.18^{c}	2.87± 0.04^{c}	49.55± 3.35^{c}	3.71± 0.06^{c}
60min	44.05± 3.18^{b}	3.30± 0.04^{b}	64.22± 3.35^{b}	4.81± 0.06^{b}
120min	62.31± 3.18^{a}	4.67± 0.04^{a}	74.45± 3.35^{a}	5.58± 0.06^{a}

a, b & c: There is no significant difference (P>0.05) between any two means, within the same column that have the same superscript letter.

Owalude and Tella [35] found that the percentage of Cr(VI) adsorption went from 52% to 88% for unmodified groundnut hulls and from 72% to 98% for modified groundnut hulls. This may be due to the greater surface area of the adsorbent and the increased availability of adsorption sites. The outcome is lower than the one obtained from this experiment.

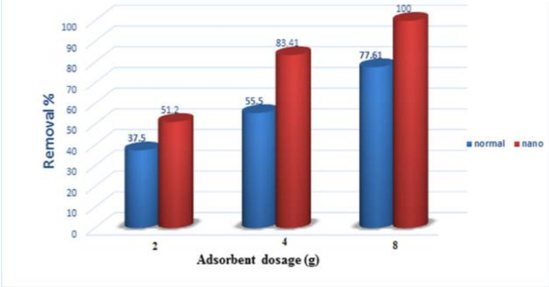


Figure (5): The impact of watermelon peel as an adsorbent for the elimination of Cr(VI) from aqueous solutions at different dosages (400 ppm Cr(VI); pH of 4, and Tem of 25°C).

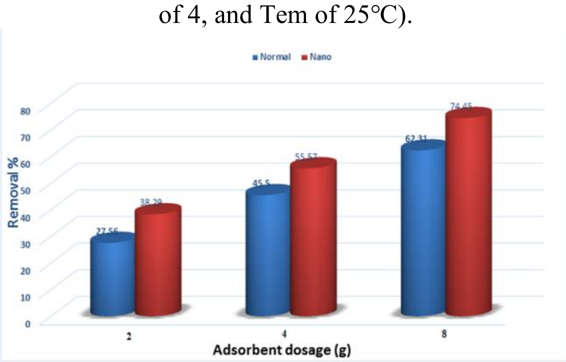


Figure (6): The impact of watermelon peel as an adsorbent for the elimination of Cr(VI) from aqueous solutions at different dosages (600 ppm Cr(VI), pH of 4, and Tem of 25°C).

3.2.3. Effect of metal concentration

The data presented in Figure (7) demonstrates the isotherm study conducted on watermelon peel. The study involved using different initial concentrations of Cr(VI) ions solution (400 and 600 mg.L^{-1}) and different doses (2, 4, and 8 g) for the watermelon peel reactions mixture, and the concentration of Cr(VI) was analyzed at various time intervals at room temperature (25.5 °C). The results showed that increasing the concentration of Cr(VI) in the solution decreased the percentage of its removal from the aqueous solutions of both normal and nanometer peels. The average removal percentage reached 77.61% and 100%, respectively for the concentration of 400 ppm while 62.31 and 74.45% for 600 ppm. For both normal and nanometer peels, respectively. These findings are consistent with those reported by **[31].**

At the optimum concentration of 400 mg/L, the ratio of metal ion moles to adsorbent surface area was significant, ensuring continuous adsorption. At greater concentrations, the surface that attracts and holds molecules becomes wholly filled, and the movement of ions from the main solution to the surface of the adsorbent reduces **[29].**

El-Tawabty *et al.* [37] used both regular and nanometer banana peels to adsorb Cr(VI) from water-based solutions; at 400 ppm, the average removal percentage was 41.9 and 65.3%, and at 600 ppm, it was 39.2% and 56.5%. Compared to what was accomplished in this experiment, the results are lower than those achieved in this experiment.

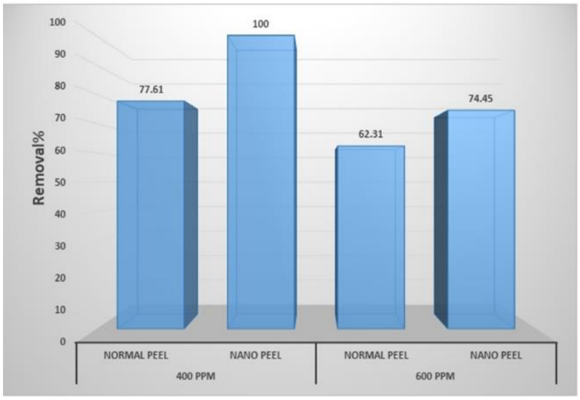


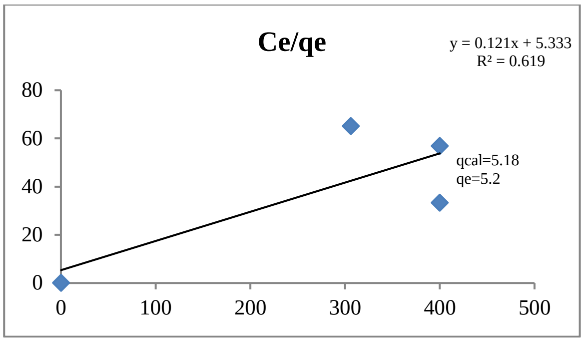
Figure (7): Effect of metal concentration on removal % from aqueous solution using watermelon peel.

3.3. Langmuir isotherm model

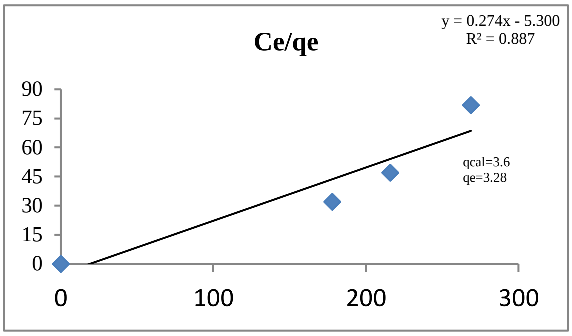
Figures (8 and 9) depict the Langmuir adsorption isotherm model applied to the adsorption of Cr(VI) at concentrations of 400 and 600 ppm onto watermelon peel. The adsorption results are consistent with the Langmuir isotherm model. The R2 values indicate that the Langmuir isotherm model describes the adsorption data well, and the adsorption of Cr(VI) onto watermelon peel is good. Several investigations indicate that the Langmuir model is better suited for modeling the adsorption isotherm of Cr(VI) onto different adsorbents **[11].**

3.4 Removal percent of Cr(VI) from tannery wastewater using normal and nano-size watermelon peel.

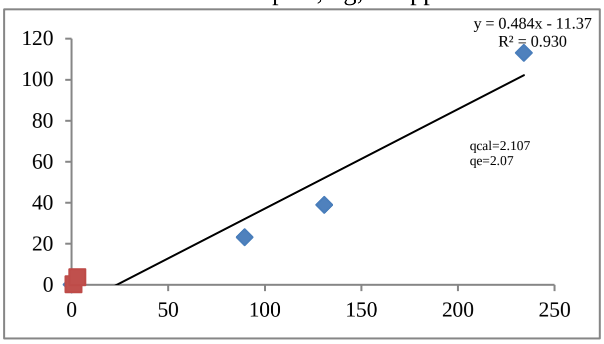
Under the impact of the ideal conditions found in this study, tanneries' water, which contains an estimated 1380 mg L-1 of Cr(VI), was utilized to assess the effectiveness of employing watermelon peels in normal and nano-metric size Cr(VI) concentration, contact time, and adsorbent weight). The outcomes demonstrated that watermelon peels of any size, whether regular or nano, had a greater capacity to absorb Cr(VI), as shown in figure (10), as evidenced by the adsorption efficiency reaching 82.53 and 95.77% for normal and nano-metric peels, respectively. This work is compatible with the case study of a low-cost sorbent's ability to remove Cr(VI) from tanneries' effluent **[23]**.



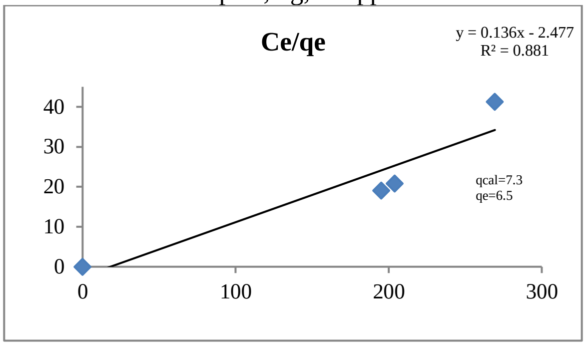
Normal peel, 2g, 400ppm



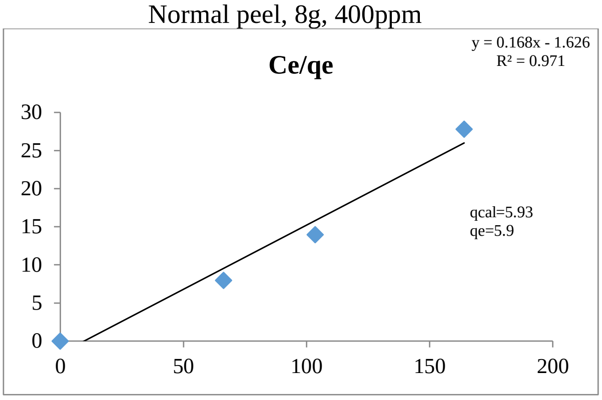
Normal peel, 4g, 400ppm



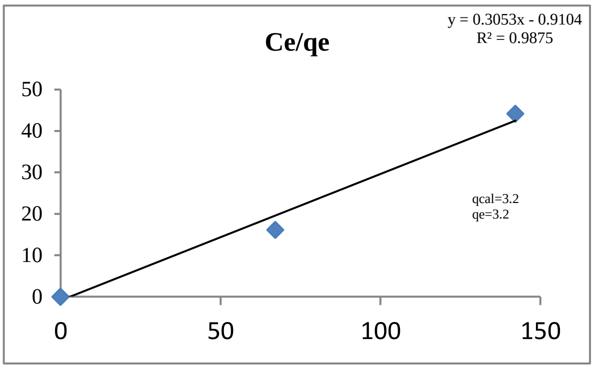
Normal peel, 8g, 400ppm



Nano peel, 2g, 400ppm



Nano peel, 4g, 400ppm



Nano peel, 8g, 400ppm

Figure (8): Model for Langmuir adsorption of 400 ppm Cr(VI) onto watermelon peel.

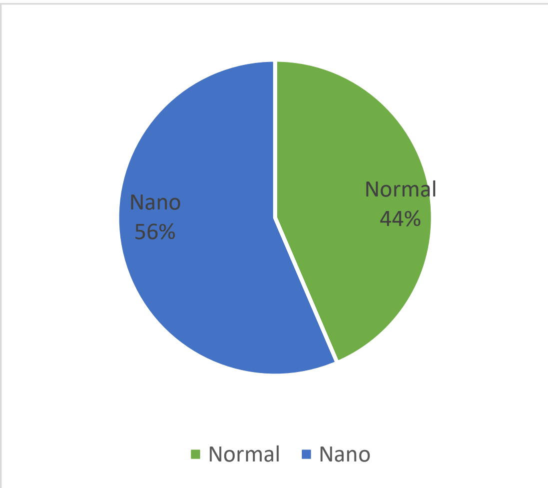


Figure (10): Cr(VI) removal percentage from tannery effluent using conventional and nano watermelon peels.

4. CONCLUSION

Cr(VI) is a hazardous and extremely poisonous contaminant. High concentrations and extended exposure can result in genotoxic and cytotoxic processes that damage DNA, lipids, and proteins in addition to oxidative stress; thus, in the end, it results in death. Therefore, the environment must be preserved by removing Cr(VI) from wastewater resulting from chrome tanning. It is worth mentioning that watermelon peel nanoparticles function well as adsorbents for removing Cr(VI). It was observed that use of watermelon peels of normal powder and nanopowder improved the adsorption efficiency up to 77.61% and 100%, respectively, at an aqueous solution of 400 ppm of Cr(VI), pH 4, the amount of adsorbent was 8 gram/Liter, the temperature was 25 °C and the contact time was 120 minutes.

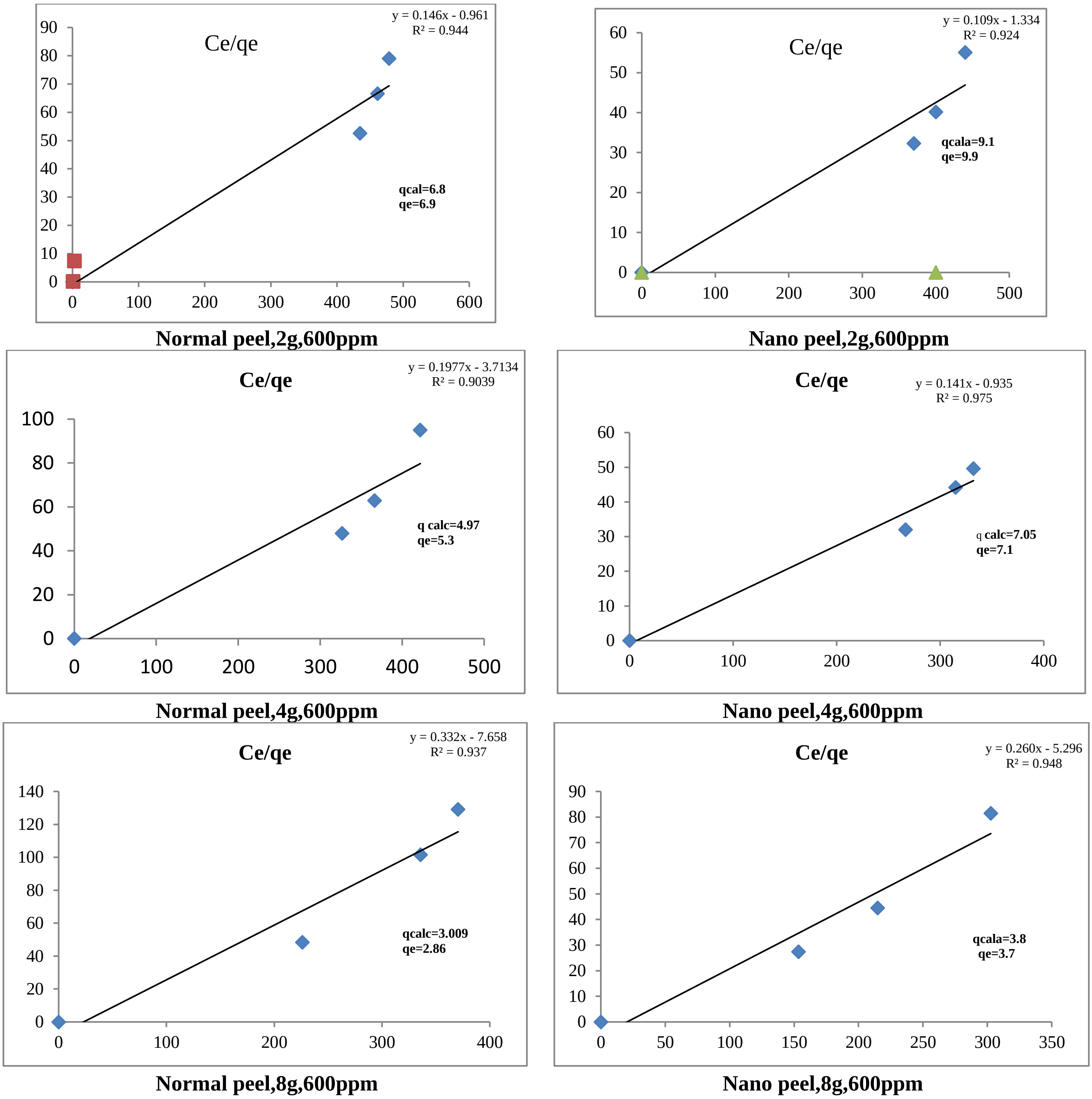


Figure. (9): Model for Langmuir adsorption of 600 ppm Cr(VI) onto watermelon peel

Also, the watermelon peels of normal powder and nanopowder improved the adsorption efficiency up to 62.31 and 74.45%, respectively, at an aqueous solution of 600 ppm of Cr(VI), pH 4, the amount of adsorbent was 8 gram/Liter, the temperature was 25 °C and the contact time was 120 minutes. Furthermore, the results indicated that watermelon peels, regardless of their size (normal or nano), had a higher ability to absorb Cr(VI). This was supported by the adsorption efficiency, which reached 82.53% and 95.77% for normal and nano-sized peels, respectively. Therefore, we recommend using nano watermelon peels since they improve adsorbing Cr(VI) efficiency in a shorter period compared to regular-sized peels. Also, the isotherm model from Langmuir and the data on adsorption are strongly associated.

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

Ethical approval

Not required

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Not applicable

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Not applicable

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