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The ability of Corn waste products to adsorb lead ions from the industrial wastewater

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Abstract

One of the results of industrial oil activity in Iraq is the high rates of pollution with heavy metals associated with this activity. Heavy metals pollution has a serious environmental problem as a result of the threat it poses to natural water resources, thus they become very dangerous to both aquatic and terrestrial life. Heavy metals have slow and non-infinite toxicity to the environment, as they are not biodegradable; therefore, the bio-adsorption technology using agricultural waste products such as Corn Husk and Corn Cob waste products becomes contemporary aspirations. The experiments of adsorption of lead ion by the Corn Husk and Corn Cob were done in the batch experiment and different influencing factors, such as (time, mixing speed, pH, and temperature) was studied for getting the optimum condition in the adsorption process. The adsorption studies showed that the capacity of the Corn Cob to adsorbed lead ions from the industrial wastewater samples more than the capacity adsorption of the Corn Husk that was 2.7042 mgg^{-1}, 79.05% under optimized conditions 20 minutes, 100 rpm, pH 5.5 and 55ºC, while the adsorption capacity of the Corn Husk was 0.7109 mgg^{-1} , 55.38% under optimized conditions 30 minutes, 100 rpm, pH 4.5 and 15ºC. A characterization study using the Fourier-transforms infrared spectroscopy (FT-IR) and Scanning Electron Microscope (SEM) indicated a good ability of Corn waste products to adsorb Lead, where they have many functional groups can help in adsorption and they showed morphological changing after adsorption of Lead as indicated by SEM images.

Key words: Corn Cob, Corn Husk, Lead, adsorption, FT-IR, SEM

Introduction

Lead is a well-known venomous heavy metal in the environment, it reported in a priority list of dangerous metal, that it can cause high public health risks at low concentrations, particularly for children (Wilson, Hou, & Meng, 2015). The main sources of lead pollution in the environment are from ore and metals processing, in addition to the leaded flying gasoline (Lin et al., 2011). Nowadays contamination by lead has become a dangerous phenomenon as a result of its use in many industrial activities, as a response to the dramatic increase in the number of people on the earth (Muedi, 2018). Because lead cannot be degraded by microbial activity, it is present in the environment and accumulates in soil, water and sediments because of its sedimentation, leaching, and erosion (Wilson, Hou, & Meng, 2015). Therefore, it has become important to find a solution to preserve the environment from such pollutants. Previously, they were depending on the traditional method to remove pollutants, like evaporation, membrane filtration, detoxification, clotting, and chemical flocculation, an ion exchange, electrodialysis and reverse osmosis. However, there are many drawbacks to these methods including high-energy consumption, work on high concentrations of pollutants as well as environmentally unwanted byproducts (Ziarati et al., 2018a). Several modified and sophisticated techniques have emerged, including many methods of biological treatment to improve the environment contaminated with heavy metals (Jaafar, 2020). Biologically the adsorption method using agricultural wastes products is an efficacious and economical strategy in eliminating heavy metals, as it has many advantages: including low cost, high efficiency, the minimum amount of unwanted waste, and the possibility of recycling it. The principle of adsorption technique is the interaction between the inactive and non-living matter of biological origin and metal ions in aqueous solution to adsorb and collect metal ions by adsorption, ion exchange, complexity on the surface and deposition (Ziarati et al., 2018b). Consequent to the low price of agricultural waste products, its use as a bio-absorbs has become common and widely used in removing heavy metals from drinking water or wastewater. There are different agriculture waste products have been investigated to their ability to use as a bio-absorbs, and the Corn waste products are one of the promising ones as referring in the previous studies (Muthusamy & Murugan, 2016) (Prasanna, 2019) (Victorino et al., 2019). Dependingly the present work aims to apply waste products of Corn to remove Lead from contaminated wastewater based on the laboratory experiment data, which included determining the ideal conditions for Corn residues to increase their efficiency in lead adsorption.

Materials and methods

Sample collection

Corns samples were collected from Corn farms in southern Iraq, Corn was put in clean plastic and transfer to the lab.

Preparation of Adsorbent

The adsorbent was prepared as follows: Cons firstly washed with distill water and left to dry on the immaculate table at room temperature. Parts of Corn, which using as adsorbent (Corn Husk and Corn Cob) have crushed by the electrical machine and they sieved by using 60μ mesh sizes.

Adsorbate solution

A lead stock solution made by dissolving 1g of lead nitrate in 1L of distilling water, a series of dilutions carried out on the standard lead solution using distilled water to obtain the required lead concentration (25 mgL^{-1}). 0.1M Hydrochloric acid or 0.1M Sodium hydroxide solution was used to adjust the pH of the solution to (4.5-8.5).

Adsorption experiments

To determine the susceptibility of the corn waste products to adsorbed the lead ions, batch experiment was used, taking into consideration several conditions to determine the optimal conditions for adsorption such as contact time(min), pH, temperature(ºC) and the mixing speed(rpm). 50mg of adsorbate mixed with 15ml of lead solution in the conical flask, the mixture was stirred at 50- 200 rpm and 15-55 °C. The contact time range from zero to 90 min and the pH range from4.5-8.5. Sample solutions were taken at intervals and filtered mixtures through Whitman filter paper No. 40 to fix the residual from the Pb (II) ions by using the Atomic Adsorption spectrophotometer (AA7000-Shimadzu) (Mohammadi et al., 2017).

The fraction of Pb (II) ions removal was gained using the Mathematical equation (1) and the total of Pb (II) ions adsorbed (mg/g biosorbent) was considered using the Mathematical equation (2):

$$\%Removal = \{(C_o - C_e) / C_o\} * 100 \qquad (1)$$

$$q_e = (C_o - C_e)V / W \qquad (2)$$

Where C_o and C_e (mgL^{-1}) are the first and final concentration of Pb (II) ions in the liquid-phase of the solution. V(mL) is the volume of the solution, W(g) is the biomass of adsorbent used and q_e ($mg\ g^{-1}$) is the amount adsorbed (Onwordi et al., 2019).

FT-IR- analysis

The infrared spectrum (FT-IR) (FT-IR-8400s type Shimadzu) was used to describe the active groups present in the adsorbed surfaces using the wave number range of 200-4000 cm^{-1}, using a disk of potassium promide.

SEM analysis

The Scanning electron microscope (SEM) was done to study the surface morphology of the Corn studied parts. During the examination, the samples were installed on a copper stand with double-sided tape. The images were taken with several magnifications of × 800 - × 7500.

Result and discussion

Characterization of Adsorbent

FT-IR analysis

Figure1 shows the infrared spectrum of Corn Husk powder at a range of 200-4000 cm^{-1}. The chemical composition of the corn is 82.7% carbohydrates and 6.6% lignin (Fadhil & Eisa, 2019), The figure shows the presence of several packages due to the presence of different groups, where we notice the emergence of a beam at 3337 cm^{-1}, which is attributed to the hydroxyl groups, whereas the bundle appears at 2920, 2897 cm^{-1} is attributed to the stretch frequency of the C-H group, the carboxyl group appears at a wave number of 1732 cm^{-1} in addition to the bundle emergence at 1639 cm^{-1} and 1604 cm^{-1}, which is due to the groups of C = C and C = N, which are included in the composition of cellulosic material, while polar groups with single bonds such as C-O and C-N appears at 1249 cm^{-1} and 1319 cm^{-1}.

Figure 2 represents the analysis of infrared spectrum, of Corn cob powder, the packages composition of the study material as follows: the hydroxyl group appears at the wave number 3255 cm^{-1}, whereas the Alphatic group of C-H appears at 3900 cm^{-1}, and the carbonyl group C = O appears at 1739 cm^{-1} as well as the appearance of a C = C and C = N groups at amplitude fluctuation 1604 cm^{-1}. Polar groups with single bonds such as C-O and C-N appear at 1253 cm^{-1} and 1319 cm^{-1}. Altogether these groups have the capability to bind with lead ions in the different processes as physical or chemical adsorption (Edbert & Akunna, 2017).

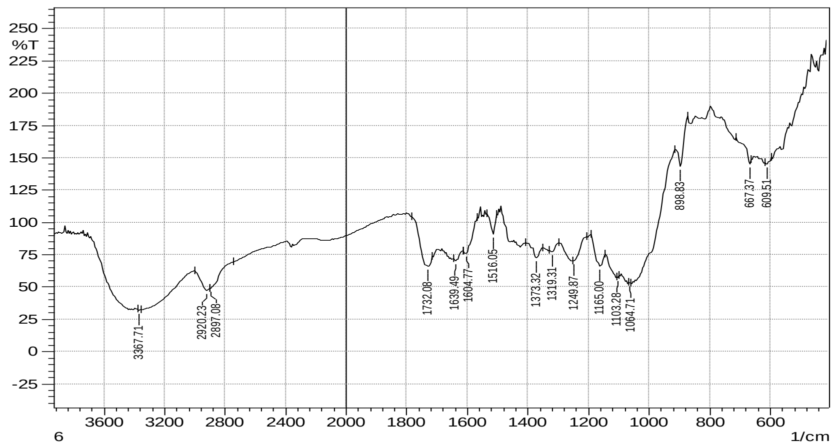

Figure 1. FT-IR spectra of Corn Husk

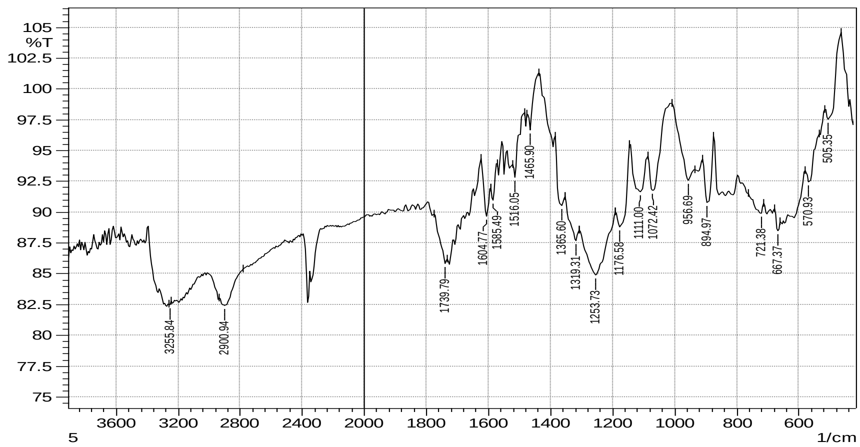

Figure 2. FT-IR spectra of Corn Cob

SEM analysis

An electron microscopy technique (SEM) used to distinguish the external morphology of both Corn Husk and Corn Cob before and after the adsorption the lead ions, and the results are shown in Fig3. According to the results obtained from the pictures, there are clear differences in the topography of the surface of both the Corn Husk (fig 3 A and B), and Corn Cob (fig.3 C and D) before and after adsorption. The results of the electron microscope of both the raw Corn Husk and Corn Cob show the presence of a non-porous fibrous form (fig.3A and B), while the surface after the adsorption process becomes spongy like-porous structure with the presence of several interconnected channels (fig.3 C and D). The adsorption process encourages modification of the surface structure of the raw materials in order to prepare the surface for receiving the absorbent material (Özsin et al., 2019).Previous works explain the surface structure of the Corn material and the results is in consistent with the present results (Anukam et al., 2017 and Özsin et al., 2019).

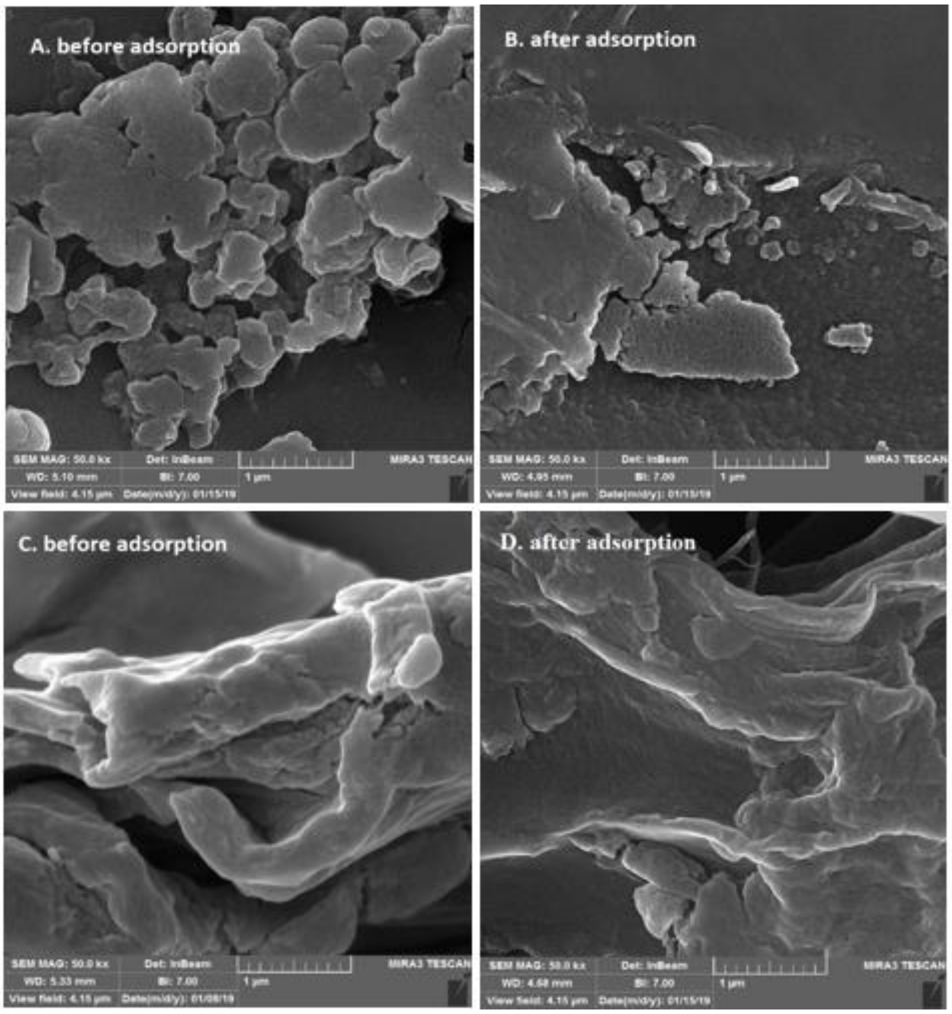

Figure 3. The Scanning electron microscope image of the Corn Husk, A before adsorption and B after adsorption, and Corn Cob, C before adsorption and D after adsorption.

Batch Method Adsorption Studies

All adsorption experiments were conducted at room temperature with a shaking speed of 130. Several factors affecting the adsorption process have been studied, such as contact time, mixing speed, pH, and temperature.

The influence of contact time in the adsorption efficiency

Table 1 shows the effecting of contact time in the adsorption ability of Corn Husk and Con Cob, results indicated that the best adsorption by the Husk of Corn occurred at the time 30min, which reached 0.114 mgg^{-1} with the percentage (15.22%). During 50-90min the equilibrium occurred where the adsorption capacity was 0.111mgg^{-1} and the percentage was (14.82%). The higher adsorption by Corn Cob occurred during 20min of contact time, where the adsorption capacity was 0.102 mgg^{-1} with the percentage (13.68%). The equilibrium occurred during (30- 90min). Increase adsorption with time indicated that the adsorption process is time dependent (Jaafar, 2020), and the reaching to the equilibrium by the subject time can be explanation by saturation of the active sites that further adsorption can not occur (Victorino et al., 2019).

Table 1. The adsorption of Lead at different contact times (min)

Times (min)	Weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption percentage (%)
	Corn Husk	
0	0.038	5.16
5	0.083	11.08
10	0.084	11.27
20	0.094	12.65
30	0.114	15.22
40	0.112	15.02
50	0.111	14.82
60	0.111	14.82
90	0.111	14.82
	Corn Cob	
0	0.009	1.22
5	0.026	3.50
10	0.039	5.26
20	0.102	13.68
30	0.101	13.50
40	0.101	13.50
50	0.101	13.50
60	0.101	13.50
90	0.065	8.77

Effect of mixing speed in the adsorption efficiency

Table 2 shows the results recorded by the experimental study of the influence of shaking speed on the bio-adsorption process of Corn Husk and Corn Cob. The results show that the highest bio-adsorption of lead ions by the Husk of Corn was at the speed of shaking 100rpm 0.179 mgg^{-1} with percentage 23.95%, Whereas, the next increase in speed led to a decrease in the adsorption. Therefore, it can be considered that the adsorption of Lead ions by the Husk of corn reached to the stable value at this velocity of shaking. The increase in speed has an effect on increasing adsorption within certain limits, and the increase in speed higher than those limits are routine and have no significance, and in some case lead to decrease the adsorption(Muthusamy & Murugan, 2016). By increasing the speed, both the adsorbate and the adsorbent particles reach their top speed, which leads to the separation of the adsorbed molecules with weak bonds on the adsorbent surfaces (Kus, 2015). The Corn Cob showed the same pattern in related to the influence of the shaking speed on the adsorption process, with a difference in the amount and percentage of adsorption (table2), but the highest adsorption was also with speeding 100rpm.

Table 2. The adsorption of Lead at different mixing speed (rpm)

Mixing speed(rpm)	Weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption percentage (%)
	Corn Husk	
50	0.171	22.84
100	0.179	23.95
150	0.178	23.75
200	0.154	20.61
	Corn Cob	
50	0.082	10.93
100	0.117	15.61
150	0.068	9.17
200	0.016	2.24

Effect of pH in the adsorption efficiency

The results of study the influence of pH in the adsorption of lead ions by the Corn Husk and Corn Cob illustrated in the table3. The results showed that the adsorption of lead ions increase by increasing the pH of solutions for both of studying materials. The maximum adsorption percentage recorded in the pH range between 4.5-5.5 (39.25% and 67.197%) respectively. The pH is considered one of the highly influencing issues in the adsorption process, as it determines the nature of the adsorbed surface, such as surface charges, and its ability to ionize in aqueous solutions (Alghamdi et al., 2019). The cellular wall of many plants contains many compounds with effective negatively charged groups such as carboxyl, sulfaheidyl and phosphate, so it is expected to form hydrostatic attraction with the metal ions. The low adsorption in the case of acidic pH lower than the pH 4 can explain according to the following: in the acidic medium, there is competition for effective sites on the adsorbed surface between protons and metal ions. As the pH increase, the competition will decrease and available proton free effective sites and thus the sites become free and ready to bind with the positive charge metal ions(Alghamdi et al., 2019). Since , at pH>7, Pb metal ions form sediment due to the great concentrations of hydroxyl ions in the liquid phases(Hayati et al., 2019), lead to precipitate from the solution, making the adsorption studies impossible, so that pH= 4.5 and 5.5 was selected as optimum value for the heavy metal ions removal by Corn Husk and Corn Cob. The results of the present study are consistent together with (Shen et al., 2018) and by different studied recorded in the book chapter of (Sadegh & Mazloumbilandi, 2018) as well as with (Sheku Alfred Kanu, Mambo Moyo, Caliphs M. Zvinowanda, 2015)

Table 3. The adsorption of Lead at different pH value

pH	Weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption percentage (%)
	Corn Husk	
4.5	0.294	39.25
5.5	0.146	19.58
6.5	0.179	23.95
7.5	0.649	86.55
8.5	0.619	82.64
	Corn Cob	
4.5	0.450	60.06
5.5	0.503	67.19
6.5	0.014	1.97
7.5	0.546	72.80
8.5	0.546	72.87

The influence of Temperature in the adsorption efficiency

Table 4 shows the results of the study the effecting of temperature in the adsorption of Lead ions by both the Corn Husk and Corn Cob in the range of temperature (15-55 ºC). In related to the Corn Husk, results indicated decrease the absorption of lead ions by increasing the temperature, where the adsorption percentage and adsorption amount of the temperature range (15-55ºC) as follows: 15>25>35>45>55. Adsorbed particles tend to detach from the adsorbent surface with the temperature increasing and because the adsorption is an exothermic process (Fadhil & Eisa, 2019). Present results is in agreement with (Nwodika & Onukwuli, 2017)and (Akalin, Hiçsönmez, & Yilmaz, 2018). Corn Cob recorded different results, where the highest adsorption was recorded at 55ºC (9.52% and 0.071 mgg^{-1}), and these results is in agreement with (Dharmendirakumar et al., 2015) and (Batool et al., 2018). The increase in temperature increases diffusion of adsorbent internal particles, which creates many free adsorption sites. Thus, the high temperature contributes to increasing the adsorption efficiency of the adsorbed surface (Geetha and Belagila, 2013).

Both of Corn Husk and Corn Cob were used for practical application of their ability to remove pollutants under optimal conditions for Lead adsorption, which was reached from studying many factors that affect the adsorption process as discussed above. The adsorption ratio of Lead ions was 67.19% and 39.25% by Corn Cob and Corn Husk respectively (Table5).

Table 4. The adsorption of Lead at different temperature (ºC)

Temperature(ºC)	Weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption percentage (%)
	Corn Husk	
15	0.207	27.61
25	0.200	26.76
35	0.112	14.95
45	0.114	15.22
55	0.143	19.12
	Corn Cob	
15	0.018	2.51
25	0.017	2.38
35	0.018	2.41
45	0.040	5.36
55	0.071	9.52

Table 5. The Absorption of lead in the aqueous solutions by Corn waste products in the optimum condition

Adsorpe Surface	pH	Time (min)	Temp (°C)	Mixing speed (rpm)	Weight capacity of Adsorption mgg^{-1} (qe)	Adsorbed ratio (%)
Corn Cob	5.5	20	55	100	16.799	67.19
Corn Husk	4.5	30	15	100	9.812	39.25

Application of the ideal condition to real samples

The application on the industrial sample is one of the most important factors that considered for any solid phase used as an adsorbent in the removal of any pollutant. The industrial sample in the current study was collected from the site of Nahr Binomar in Basra governorate Southern of Iraq.

Table 6 summarizes the results of applying corn waste products to remove Lead from the real sample. The capacity adsorption in the optimal parameters by the Corn Cob was high than Corn Husk (2.7042 mgg^{-1}, 79.05% and 0.7109 mgg^{-1}, 55.38%) for Corn Cob and Corn Husk respectively. Through the results of the practical application of corn waste to remove pollutants, and through the high rate of lead adsorption recorded through this experiment, we can say that these wastes have a great potential to remove such pollutants. The attractive features of Corn are that it is commercially available, effective, and low-cost. The current finding is in agreement with (Opeolu et al., 2009)

Table 6 The Absorption of lead in the industrial sample of Corn waste products in the optimum condition

Adsorbent	pH	Time (min)	Temperature °C	agitation speed (rpm)	Weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption Ratio (%)
Corn Cob	5.5	20	55	100	2.7042	79.05
Corn Husk	4.5	30	15	100	0.7109	55.38

Conclusions

This study indicates the ability to use the corn plant residues such as Corn Cob and Corn Husk as an efficient material for adsorption of lead ions. As the results showed a high capacity to adsorption in a short time as a cheap material, available in nature and considered environmentally friendly. Since Corn waste products have the potential to remove Pb^{2+} from aqueous solutions and industrial effluents, it implies that it may also decontaminate wastewaters containing other divalent metal ions such as Zn^{2+}, Cd^{2+}, amongst others. There is, therefore, the need for more extensive research on the possibility of removing such metals using other crop residues since typical wastewaters contain mixed metal ions. This may increase the extent of use and applicability of the residues in wastewater remediation.

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قابلية مخلفات الذرة على امتزاز أيونات الرصاص من مخلفات مياه الصرف الصناعية

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المستخلص

يعد التلوث بالمعادن الثقيلة في العراق من أبرز المشاكل المرتبطة بالصناعات النفطية. ان تلوث المياه بالمعادن الثقيلة يعتبر من المشاكل البيئية الخطيرة وذلك نتيجة" لما يسببه من تهديد لمصادر المياه الطبيعية والذي بدوره يشكل مصدر من مصادر الخطورة لكل من الحياة على اليابسة والحياة المائية. ان للمعادن الثقيلة تأثير سمي لامتناهي وبطيء على البيئة كونها غير قابلة للتكسير الحيوي وبذلك تعتبر تقنية الامتزاز الحيوي باستخدام البقايا النباتية كبقايا كل من كالح الذرة واوراق الكالح من الحلول المعاصرة كونها غير مكلفة وصديقة للبيئة ومتوفرة بكثرة وسهولة تطبيقها. في الدراسة الحالية تم اجراء تجربة امتزاز ايونات الرصاص بواسطة كل من كالح الذرة واوراق الكالح في ظروف مختلفة تحت عوامل متعددة شملت (الزمن، سرعة الرج، الدالة الحامضية، ودرجة الحرارة) وذلك للحصول على الظروف المثلى بالنسبة لعملية الامتزاز. بينت النتائج ان قابلية كالح الذرة لامتزاز عنصر الرصاص أكبر من قابلية ورق الكالح حيث سجلت قابلية امتزاز $2.7042 mgg^{-1}$ ونسبة مئوية 79.05% للرصاص من مخلفات المياه الصناعية الملوثة تحت الظروف المثلى للامتزاز لتلك العوامل المدروسة حيث كانت كالتالي: الزمن المثالي 20 دقيقة، سرعة الرج 100 دورة /دقيقة، الدالة الحامضية للامتزاز كانت عند الاس الهيدروجين 5.5، درجة حرارة المثلى 55 درجة مئوية. بينما سجلت قابلية ورق الكالح $0.7109 mgg^{-1}$ ونسبة مئوية 55.38% لامتزاز عنصر الرصاص من مخلفات المياه الصناعية تحت الظروف المثلى للامتزاز كالتالي: الزمن المثالي 30 دقيقة، سرعة الرج 100 دورة /دقيقة، الدالة الحامضية للامتزاز كانت عند الاس الهيدروجين 4.5، درجة حرارة المثلى 15 درجة مئوية. وباستخدام التقنيات الحديثة كطيف الاشعة تحت الحمراء(FT-IR) والمجهر الالكتروني (SEM) حيث بينت قابلية جيدة لبقايا نبات الذرة لامتزاز ايونات الرصاص، ذلك من خلال وجود العديد من المواقع الفعالة يمكنها المساعدة في الامتزاز كما وبينت وجود تغيرات مظهرية بعد عملية الامتزاز لأيونات للرصاص وذلك كان واضحا" من خلال صور المجهر الالكتروني.

الكلمات المفتاحية: -كالح الذرة، اوراق الكالح، الرصاص، الامتزاز، FT-IR،SEM .