Removal of heavy metal ions from some wastewater by using different agricultural wastes

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ABSTRACT

Industrial wastewaters are deposed into the River Nile without any treatment. High concentrations of some heavy metals i-e Ni^{+2}, Cu^{+2}, Zn^{+2}, CO^{+2} and Cd^{+2}, promate the growth of gelatinous masses and hence cause industrial and agriculture problems. Polluted water may cause many health problems such as liver and kidney diseases. The aim of the present study is an attempt to removal heavy metals in industrial wastewater. Also, evaluation of some agricultural wastes such as orange peels, banana peels and leaves of date trees as biosorbent to remove the heavy metals which presenting from wastewater such as nickel (Ni^{+2}), copper (Cu^{+2}), zinc (Zn^{+2}), lead (pb^{+2}), cobalt (CO^{+2}) and cadmium (Cd^{+2}) by using prepared active carbons from the above-mentioned materials of different agricultural wastes in batch adsorption process. Proximate, chemical components of lignocellulosic wastes under investigation were determined. Also, physical and chemical preparation of wastewater and the produced active carbons from different agro-wastes were evaluated. On the other hand, the activated carbons from different agro-wastes were used as biosorbents for removal of some above-mentioned heavy metals before deposing in wastewater.

Keywords: Agriculture Wastes; Activated Carbons; Heavy Metals; Adsorption.

Introduction

Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Toxic heavy metals are considered as one of the pollutants that have the direct effect on man and animals. Industrial wastewater containing nickel, copper, zinc, lead, cobalt and cadmium, etc, for example, can contaminate River Nile and thus lead to a serious pollution problem ***(Renge et al., 2012).***

Heavy metals in the environmentsuch as water are harmful to human and environment. These heavy metals include elements like cadmium, nickel, lead, copper, zinc, manganese and cobalt etc. The presence of heavy metal results in bioaccumulation and further it can affect the biological and ecological cycles ***(Kulkarniet al., 2014).***

Agricultural wastes and by-products were found to be low cost and alternative adsorbents for the removal of heavy metal ions by adsorption processes. Agricultural wastes are rich in organic contents with a variety of functional groups which can co-operate binding of cations and anions. The other advantages of agricultural wastes like orange peel and banana peel are easily available, non-hazardous and no disposal problems ***(Lakshmipathyet al., 2015).***

Li et al., (2008)used orange peel for the removal of Cd^{+2}, Ni^{+2}, CO^{+2} and Zn^{+2} ions and they found that protonated orange peels had shown highest loading capacity compared to native peels. ***Achaka et al., (2009)*** investigated the efficiency of banana peel as a biosorbent for removal of phenolic compounds from olive mill wastewaters. Banana peel is largely composed of cellulose, pectin, galacturonic acid, hemicellulose, lignin, chlorophyll pigments and other low molecular weight compounds, including limonene. ***Layla and Ahmed (2010)*** used wastes of date palm tree leaves to remove heavy metalcations (Cu^{+2}, Cd^{+2} and Zn^{+2}) from simulated artificial wastewater using batch adsorption process. They found that date palm wastes succeeded to achieve 90% removal for Cu^{+2} ions, 57.5% for Cd^{+2} ions and 37.5% for Zn^{+2} ions within (60 min) contact time at adsorbent loading ratio of 30 g/l. ***Hossain et al., (2012)***used agricultural wastes from banana peel to produce bioadsorbent through easy and environmental friendly processes. The characterization results showed that sorbent had very high specific surface area, potential binding sites and functional groups. The optimal conditions for sorbent were found at pH 6.5, sorbent size of less than 75μ, dose of 0.5g/100ml and contact time 1h.***Moreno-Piraján and Giraldo (2012)***found that the activated carbons obtained from orange peel (ACOP) has the ability to retain Cr^{+3}, Cd^{+2},and CO^{+2} metals ions from the aqueous solutions at different concentrations. ACOP has a relatively high adsorption capacity for these heavy metals the quantities adsorbed per gram of (ACOP) at equilibrium were 28.67 mg/g for Cd^{+2}30.11 mg/g for Cr^{+2} and 45.44 mg·g–1 for CO^{+2}.***Husoon et al., (2013)*** used less expensive and much frequently available materials, orange peel and lemon peels to remove copper and lead from industrial wastewater. They found that the peels powder of both orange and lemon showed a higher capacity than fresh and dried pieces where the lemon powder has shown biosorption capacity of 72.5% and 71.3% for lead and copper, respectively. While, orange powder had a bio-removal percentage of

56.7% of lead and 34.5% for copper. ***Sridhar et al., (2014)***found that the percentage of removal of copper and lead from automotive wastewater byusing banana peels were 93.52 and 87.44%, respectively.

Jain (2015)used the various fruits and vegetable peels such as pineapple peels, potato peels, citrus fruits peels, orange peels, pomegranate peels, banana peels and tomato peels for removal of heavy metal. The extent of removal of heavy metals was found to be dependent on sorbent dose, initial concentration, pH and temperature. ***Manjuladevi and Oviuaa (2017)*** studied that activated carbons produced from cucumismelo peel (CM) was used as adsorbent to remove Cr^{+6}, Cd^{+2}, Ni^{+2} and Pb^{+2} ions from battery industry and electroplating industrial wastewater. The obtained results showed thatthe optimum adsorbent dosage, metal ion concentration and pH were found to be at 250 mg, 100 mg/L and pH 3 to 6 respectively.

The aim of the present works was to remove heavy metals of the industrial wastewater and evaluated of some agricultural by- products as biosorbent to remove the heavy metals of wastewater.

Materials and Methods

The samples were collected from industrial wastewater in Mubarak Zone (Quesna-Monofeya Governorate) two samples; were collected the first were taken after treatment and the second is before treatment bywater desalination plant.

Activated carbons from different agriculture food wastesthe activated carbons were prepared by following the one step pyrolysis method according to the methods described by **Amaya *et al.*, (2007),Zuo*et al.*, (2009) and Sugumaran *et al* ., (2012).**

Chemical composition of agricultural food wastes:-

The moisture content, crude ash, crude fat and crud protein were determined according to method described by **A.O.A.C (2010).** The total carbohydrateswere determined according to **Bernfeld (1955) and Miller (1959)**methods. The cellulose, hemicelluloses and lignin content were determined according to **Arunakumara *et al.*,** methods**(2013)**.The carbonate and bicarbonate ($CO_3^{=}$, HCO_3^{-}), chlorosity (Cl^{-}), sulphate ($SO_4^{=}$), calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium and potassium (Na^{+}, K^{+}) and ammonium (NH^{+4}) according to **APHA, (1992).** The nitrate (NO_3^{-}) was determined according to **Mullin and Riley (1955)** methods.The concentration of carbonates and sodium adsorption ratio were determined according an experimental parameter by **Muhammad and Saqib (2014).**

Removing heavy metals by using activated carbons:-

Different adsorbent weights of prepared activated carbons from orange peel, banana peel and leave of date trees with different amounts of each one (0.4, 0.8, 1.2, 1.6 and 2g) were mixed with 40 ml wastewater and were shak at 150 rpm for 3h at 30ºC. Thewastewater were taken from different sources. The concentrations of each heavy metal such as nickel, copper, zinc, lead, cobalt and cadmium were determined by using atomic adsorption spectrophotometer, model 2038. The absorbed values of the different studied heavy metals ions were calculated according to **Sugumasan*et al.*,**methods **(2012).**

Results and Discussion

Chemical composition of agricultural food wastes under investigation:-

The biochemical analysis results of orange peel, banana peel and leave of date trees are presented in **Table (1).** From the obtained data the proximate analysis, such as moisture and ash content were high in orange peel (10.12±0.18g/100g) and banana peel (9.08±0.17g/100g) but banana peel content high crude fat (6.30±0.05 g/100g). While, the crude protein was found high in leave of date trees (8.26±0.60g/100g).On the other hand, the carbohydrate content of different agro-wastes under investigation was found to be 58.10±0.10, 42.20±0.10 and 46.32±0.10 g/100gfor orange peel, bananas peel and leave of date trees, respectively. These results are in agreement with those reported by **Kamsonlian *et al.*, (2011)** and **Sugumaran *et al.*, (2012).** Also, the cellulose, hemicelluloses and lignin contents were found to be 14.28±0.49, 4.10±0.49 and 4.15± 0.12 g/100g for orange peel, while, these values were 12.60±0.49, 9.20±0.49 and 8.32±0.12 g/100g for banana peel. But the mean values were found to be 17.20±0.49, 9.42±0.49 and 1.53±0.12 g/100g for leave of date trees, respectively. Although, the obtained results are closed to those reported by **Budinova*et al.*, (2006), Hossain*et al.*, (2012)** and**Sugumaran *et al.*, (2012).**They obtained about similar results.

Table 1. Chemical composition of agricultural food wastes (g\100g) on the dry weight basis

Components	Lignocelluloses wastes (wt % dry basis)		
	Orange peel	Banana peel	leave of date trees
Moisture	10.12[a]± 0.18	5.30[b] ± 0.18	6.10[c]± 0.18
Crude ash	5.10[c]± 0.17	9.08[a]± 0.17	7.04[b]± 0.17
Crude fat	2.15[c]± 0.05	6.30[a]± 0.05	4.13[b]± 0.05
Crude protein	2.00[b]± 0.60	7.00[b]± 0.60	8.26[a]± 0.60
Carbohydrate	58.10[a]± 0.10	42.20[b]± 0.10	46.32[a]± 0.10
Cellulose	14.28[b]± 0.49	12.60[b]± 0.49	17.20[a]± 0.49
Hemicelluloses	4.10[b]± 0.49	9.20[a]± 0.49	9.42[a]± 0.49
Lignin	4.15[b]± 0.12	8.32[a]± 0.12	1.53[c]± 0.12

Values are mean ± standard deviation of three replicates

Physical and chemical parameters of wastewater under investigation:-

The physical properties such as color, odor,turbidity, transparency and pH for different sources of wastewater before and after filtration by various plant by products are summarized in **Table (2).** Industrial wastewater under investigation (Mubarak Zone region- Quesna) before and after treatment in the industrial station were evaluated. The obtained results for color, odor, turbidity and transparency were found to be muddy, disagreeable and turbid, respectively before filtrationalso, but after filtration these parameters were found to be clear, agreeably and clear, respectively.

Table (2): Evaluation the physical parameters of industrial wastewater before and after treatments

Parameters	Industrial wastewater			
	Before treatment		After treatment	
	Before filtration	After filtration	Before filtration	After filtration
Color	Muddy	Clear	Muddy	Clear
Odor	Disagreeable	Agreeable	Disagreeable	Agreeable
Turbidity	Turbid	Clear	Turbid	Clear
Transparency	Turbid	Clear	Turbid	Clear

Also, the chemical characterization of the above all samples from different sources were evaluation i.e. electrical conductivity, (E.C.) soluble anions ($CO_3^{=}$, HCO_3^-, Cl^-, $SO_4^{=}$), soluble cations(Ca^{+2}, Mg^{+2}, Na^+ and K^+), residual sodium carbonate (RSC), and sodium adsorption ratio (SAR) as well as concentration of NH^{+4} and NO_3^-. The obtained data are recorded in **Table (3).** From the obtained results, the electrical conductivity of industrial wastewater from different source samples was higher than (3.44, 14.77 ds/m). Also, soluble anions such as $CO_3^{=}$, HCO_3^-, Cl^- and $SO_4^{=}$ were estimated for different water samples under investigation. The mean values of soluble anions, $CO_3^{=}$, HCO_3^-, Cl^- and $SO_4^{=}$ were found to be 0.00, 4.06, 11.92 and 11.90 meq/L for Mubarak Zone region industrial wastewater before treatment, respectively. While, these values of the other samples after treatment were 0.00, 13.87, 44.58 and 43.20 meq/L for soluble anion, respectively. Also, **Tables (3)** illustrated the soluble cations such as Ca^{+2}, Mg^{+2}, Na^+ and K^+, residual sodium carbonate (RSA) and soluble adsorption ratio (SAR). The mean values of these cations were found to be treatment 7.14, 2.32, 18.26, 0.15, 0.00 and 8.40 meq/L for industrial wastewater after treatment, respectively. While, these values were 10.00, 1.38, 90.00, 0.28, 0.00 and 37.73 meq/L for industrial wastewater before treatment, respectively. While, NH_4^+ and NO_3^- contents were found to be 5.11 and 15.89 mg/Lfor industrial wastewater after treatment and were found to be 8.40 and 10.85 mg/Lfor industrial wastewater entrance of the treatment plant and factories leather waste and food , respectively. These results are in agreement of those reported by **Castro *et al.*, (2011), Sugumaran *et al.*, (2012)** and **Majumdar *et al.*, (2016).**

Production of active carbons:-

Date in **Table (4)** illustrated the production of active carbons from different sources of lignocelluloses food wastes at 450ºC. From the obtained results, it can be observed that the leaves of date trees produced the highest yield of active carbon equaled to 49.28% and 78.86% at different activation of food wastes KOH and H_3PO_4respectively, in compassion compared with other agro-wastes and other activation methods. On the other hand, the yield of 35.89% was recorded in banana peel treated with H_3PO_4 followed by the treatment with KOH 25.30% in compassion with distilled wastes 25.30% as activation method (untreated). The yield of 38.49% was recorded in orange peel treated with

$H_3PO_4$and KOH respectively. These results are in accordance with those reported by **Sugumaran *et al.*, (2012).**

Initial concentrations of some heavy metals of industrial wastewater before treatment:-

The present investigation was curried out evaluate the removal of metals and heavy metals such as Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, CO^{+2} and Cd^{+2}. The samples under investigation were taken from industrial Mubarak Zone, Monofeya. The obtained results are recorded in **Table (5)**. From the above-mentioned data, it can conclude that the initial concentration of the studied heavy metals like Ni^{+2}, Pb^{+2} and CO^{+2} in wastewater were higher than the permissible leaves according to **WHO,(2006).** While, the other heavy metals such as Zn^{+2}, Cu^{+2} and Cd^{+2} were lower than the permissible levels. These results are in agreement with those reported by **Sha*et al.*, (2010)**, **Shaba *et al.*, (2014)** and **Manjuladevi *et al.*, (2017).**They reported the some treed by the treatment.

Table 3. Chemical analysis of industrial wastewater

Measurements	Entrance of the treatment plant	Factories leather waste and food
EC (ds/m)	3.44	14.77
pH	7.50	7.90
	Soluble Anions (meq./L)	
$CO_3^=$	0.00	0.00
HCO_3^-	4.06	13.87
Cl^-	11.92	44.58
$SO_4^=$	11.90	43.20
	Soluble cations (meq./L)	
Ca^{++}	7.14	10.00
Mg^{++}	2.32	1.38
Na^+	18.26	90.00
K^+	0.15	0.28
RSC	0.00	0.00
SAR	8.40	37.73
	Concentration (mg/L)	
NH_4^+	5.11	8.40
NO_3^-	15.89	10.85

Table 4. Activated carbons of agricultural food wastes at different activation methods

Agricultural food wastes samples	Activated carbons (%)		
	Activation methods		
	KOH (10%)	H_3PO_4 (10%)	Untreated distilled water
Orange peel	22.30	38.49	15.21
Banana peel	25.30	35.89	25.05
Leave of date trees	49.28	78.86	49.20

Table 5. Initial concentrations of some heavy metals of industrial wastewater

Metal ions	permissible levels (mg/L) according to (WHO, 2006)	Heavy metal concentrations (mg\L)	
		Industrial Mubarak ZoneMonofeya	
		Before	After
Ni^{+2}	0.01	3.81±0.01	1.81 ±0.01
Cu^{+2}	1.00	0.00	0.00
Zn^{+2}	1.00	0.13±0.01	0.19±0.01
Pb^{+2}	0.05	0.81±0.01	0.72±0.01
CO^{+2}	0.05	0.85±0.01	0.80±0.01
Cd^{+2}	0.05	0.00	0.00

Effect of active carbons from different agricultural food wastes on the removal of heavy metals from industrial wastewater:-

The effect of producing active carbons from different agro-food wastes on the removal of nickel (Ni^{+2}) in wastewater before and after treatment was evaluated and the obtained results are recorded in **Table (6)**. From these results, it can be generally noticed that the removal percentages of Ni^{+2}ion under different activation methods (KOH and H_3PO_4) from wastewater were increased with increasing the adsorbent dosage of the active carbons. In case of productive carbons under activation method by KOH, maximum removal percentage of nickel (Ni^{+2}) was found to 9.97% for orange peel with maximum dose (2g). But, with banana peel were significantly higher which equaled (37.80%). However, the highest level of removal percentage of Ni^{+2} in the case of active carbons produced from leaves of date trees by activation method with KOH which was 45.67% , at the same dose (2.0g) of bioadsorbent. These results are slightly different with those reported by **Moreno-piraján and Giraldo (2012)**.

Also, the removal of zinc (Zn^{+2}) from wastewater before the treatment was estimated and the obtained results are presented in **Table (7).** Under activation methods by KOH, H_3PO_4 orange peel, banana peel and leave of date trees, removal percentage of zinc (Zn^{+2}) was found to be 100.00% at dose of 2.0g. However, the removal percentage of Zn^{+2} in the case of activated carbons produced from the above-mentioned food wastes by activation method with KOH 100.00% under the same dose (1.6g) of bioadsorbent. The obtained results are close with that reported by **Ashraf *et al.*, (2011)**This peculiar nature of nickel indicates relatively higher variation in oxidation states (d8 element), in contrast to zinc (d10 element) **Rasheed *et al.*, (2013).**

The adsorption efficiency of agro-wastes on the removal of pb^{+2} ion in wastewater from Mubarak Zone region- Quesna before treatments are presented in **Table (8).** From the obtained results, maximum removal percentage of lead (Pb^{+2}) was found to be 34.57% in case of activation method by KOH from orange peel. But, with banana peel was significantly higher, which found to be 79.01% at same doses of biosorbent 2.0g. However, the highest level of removal percentage of Pb^{+2} in the case of activated carbons produced from leave of date trees by activation method with KOH was 88.89% at dose (2.0g) of bioadsorbent. The obtained results are different with those reported by **Azizi and Ghasmeni (2015).**

While, the effect of producing active carbons from different agro-food wastes in the removal of cobalt (Co^{+2}) in wastewater before pretreatment was evaluated and the results are recorded in **Table (9).**In case of activation method by KOH from orange peel, maximum removal percentage of cobalt (Co^{+2}) equaled to 44.71%, but with banana peel the vole significantly higher where it has been found to be (76.47%) at adsorbent weight of dose 2.0g. However, removal percentage of Co^{+2} reached to 96.47% at the same dose (2.0g) of bioadsorbent in the case of active carbons produced from leaves of date trees by activation method with KOH. The obtained results are in agreement with those reported by**Renge*et al.*, (2012)** who found about similar results.

Data in **Table (10)** show the effect of biosorbent produced active carbons from different agro-food wastes in the removal of nickel (Ni^{+2}) in wastewater. The maximum removal percentage of nickel (Ni^{+2}) was found to 48.07% in case of orange peel, but with leaves of date trees, were significantly lower (43.65%) at same maximum dose (2.0g). However, the highest removal percentage of Ni^{+2} in the case of activated carbons produced from banana peel by activation method with KOH which was 51.38% at the same dose (2.0g) of bioadsorbent. The obtained results are different with those reported by **Annadusai*et al.*, (2017).**.Fanatical groups most commonly implicated in such interactions include carboxylate, hydroxyl, amine and phosphoryl groups present within cell wall components such as polysaccharides, lipids and proteins**Ozer*et al.*, (2004).**

Also, the effect of produced active carbons from differentagro-food wastes on the removal percentage of zinc (Zn^{+2}) of wastewater after the treatmentwas evaluated and the obtained results are recorded in **Table (11),** by using the active carbons of orange peel, banana peel and leave of date trees. From the obtained data the maximum removal percentage of zinc (Zn^{+2}) was found to 100.00% as biosorbent at 2.0g expect leave of date trees with activation method by H_3PO_4(89.47%).However, the highest level of removal percentage of Zn^{+2} in the case of activated carbons produced from different agricultural food wastes under investigation by activation method with KOH was 100.00% at the same dose (2.0g) of bioadsorbent . The achieved results are in agreement with those reported by **Renge*et al.*, (2012)** reported about the same trend.

The removal of lead (Pb^{+2}) from wastewater by the above-mentionedsamples after the treatment by adsorption processes was evaluated and the obtained results are recorded in **Table (12).** From these data, it can be observed that the maximum removal percentage of lead (Pb^{+2}) was found to be 79.17% for orange peel. But with banana peel, this value was significantly higher (87.50 %) at some doses 2.0g. In the case of activecarbons produced from leave of date trees by activation method with KOH, the removal was percentage 88.89% at the same dose (2.0g) of bioadsorbent. The obtained results are in agreement with those reported by **Manjuladevi and Oviuaa (2017)** who observed about the same observation.

But, the effect of active carbons from different agro-food wastes in the removal of cobalt (Co^{+2}) in wastewater after pretreatment was evaluated. The obtained results are recorded in **Table (13).**

Table (6): Effect of activae carbons from different agricultural food wastes on the removal of metal (Ni^{+2}) ion from industrial wastewater before treatment

Dose (g)	Orange peel				Banana peel				Leave of date trees			
	KOH		H_3PO_4		KOH		H_3PO_4		KOH		H_3PO_4	
	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %
0	3.81 ± 0.01^{fA}	0.00	3.81 ± 0.01^{fA}	0.00	3.81 ± 0.01^{fA}	0.00	3.81 ± 0.01^{fA}	0.00	3.81 ± 0.01^{eA}	0.00	3.81 ± 0.01^{fA}	0.00
0.4	3.77 ± 0.01^{eA}	1.05	3.80 ± 0.00^{eB}	0.26	3.69 ± 0.01^{eA}	3.15	3.760 ± 0.01^{eB}	1.31	3.72 ± 0.01^{dA}	2.36	3.80 ± 0.00^{eB}	0.26
0.8	3.67 ± 0.01^{dA}	3.67	3.74 ± 0.01^{dB}	1.84	3.57 ± 0.01^{dA}	6.30	3.65 ± 0.01^{dB}	4.20	3.60 ± 0.01^{dA}	5.51	3.63 ± 0.01^{dB}	4.72
1.2	3.60 ± 0.00^{cA}	5.51	3.71 ± 0.01^{cB}	2.62	3.41 ± 0.01^{cA}	10.50	3.49 ± 0.01^{cB}	8.40	3.21 ± 0.01^{cA}	15.75	3.38 ± 0.00^{cB}	11.29
1.6	3.56 ± 0.01^{bA}	6.56	3.67 ± 0.01^{bB}	3.67	2.98 ± 0.01^{bA}	21.78	3.31 ± 0.00^{bB}	13.12	2.89 ± 0.00^{aA}	24.15	3.00 ± 0.00^{bB}	21.26
2.0	3.43 ± 0.01^{aA}	9.97	3.47 ± 0.01^{aB}	8.92	2.37 ± 0.01^{aA}	37.80	2.89 ± 0.00^{aB}	24.15	2.07 ± 0.03^{aA}	45.67	2.50 ± 0.01^{aB}	34.38

Mean of materials	Orange peel	Banana peel	Leave of date trees			
	3.64 ± 0.02^{C}	3.31 ± 0.08^{A}	3.38 ± 0.10^{B}			
Mean of treatment	KOH	H_3PO_4				
	3.30±0.07A	3.45 ± 0.06^{B}				
Mean of dose	0	0.4	0.8	1.2	1.6	2.0
	3.81 ± 0.01^{F}	3.76 ± 0.01^{E}	3.64 ± 0.01^{D}	3.47 ± 0.04^{C}	3.23 ± 0.07^{B}	2.79 ± 0.13^{A}

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

Table 7. Effect of active carbons from different agricultural food wastes on the removal of heavy metal (Zn^{+2}) ion from industrial wastewater before treatment

Dose (g)	Orange peel				Banana peel				Leave of date trees			
	KOH		H_3PO_4		KOH		H_3PO_4		KOH		H_3PO_4	
	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %
0	$0.13 \pm .01^{dA}$	0.00	$0.13 \pm .01^{eA}$	0.00	$0.13 \pm .01^{eA}$	0.00	$0.13 \pm .01^{fA}$	0.00	$0.13 \pm .01^{eA}$	0.00	$0.13 \pm .01^{fA}$	0.00
0.4	0.05 ± 0.01^{cA}	61.54	0.07 ± 0.00^{dB}	46.15	0.06 ± 0.00^{dA}	53.85	0.08 ± 0.00^{eB}	38.46	0.08 ± 0.00^{dA}	38.46	0.10 ± 0.00^{eB}	23.08
0.8	0.03 ± 0.01^{bA}	76.92	0.05 ± 0.00^{cB}	61.54	0.05 ± 0.00^{cA}	61.54	0.07 ± 0.00^{dB}	46.15	0.06 ± 0.01^{cA}	53.85	0.08 ± 0.00^{dB}	38.46
1.2	0 ± 0^{aA}	100.00	0.02 ± 0.00^{bB}	84.62	0.03 ± 0.00^{bA}	76.92	0.03 ± 0.00^{cB}	76.92	0.02 ± 0.00^{bA}	84.62	0.04 ± 0.00^{cB}	69.23
1.6	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0.02 ± 0.00^{bB}	84.62	0 ± 0^{aA}	100.00	0.02 ± 0.00^{bB}	84.62
2.0	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00

Mean of materials	Orange peel		Banana peel		Leave of date trees	
	0.02 ± 0.00^{A}		0.03 ± 0.01^{B}		0.03 ± 0.01^{B}	
Mean of treatment	KOH		H_3PO_4			
	0.02 ± 0.00^{A}		0.04 ± 0.00^{B}			
Mean of dose	0	0.4	0.8	1.2	1.6	2.0
	0.13	0.07	0.05	0.02	0.01	
	$\pm .01^{F}$	$\pm 0.00^{E}$	$\pm 0.00^{D}$	$\pm 0.00^{C}$	$\pm 0.00^{B}$	0 ± 0^{A}

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

Table 8. Effect of active carbons from different agricultural food wastes on the removal of heavy metal (Pb^{+2}) ion from industrial wastewater before treatment

Dose (g)	Orange peel				Banana peel				Leave of date trees			
	KOH		H_3PO_4									
	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %
0	0.81 ± 0.01^{eA}	0.00	0.81 ± 0.01^{fA}	0.00	0.81 ± 0.01^{fA}	0.00	0.81 ± 0.01^{fA}	0.00	0.81 ± 0.01^{fA}	0.00	0.81 ± 0.01^{fA}	0.00
0.4	0.73 ± 0.01^{dB}	9.88	0.47 ± 0.01^{eA}	41.98	0.34 ± 0.00^{eA}	58.02	0.40 ± 0.00^{eB}	54.32	0.33 ± 0.01^{eA}	59.26	0.61 ± 0.00^{eB}	24.69
0.8	0.72 ± 0.01^{dB}	11.11	0.41 ± 0.01^{dA}	49.38	0.31 ± 0.00^{dA}	61.73	0.37 ± 0.00^{dB}	50.62	0.29 ± 0.01^{dA}	64.20	0.38 ± 0.00^{dB}	53.09
1.2	0.63 ± 0.01^{cB}	22.22	0.36 ± 0.02^{cA}	55.56	0.23 ± 0.01^{cA}	71.60	0.34 ± 0.01^{cB}	58.02	0.19 ± 0.00^{cA}	76.54	0.21 ± 0.01^{cB}	74.07
1.6	0.59 ± 0.00^{bB}	27.16	0.29 ± 0.01^{bA}	64.20	0.20 ± 0.00^{bA}	75.31	0.31 ± 0.01^{bB}	61.73	0.11 ± 0.01^{bA}	86.42	0.20 ± 0.00^{bB}	75.31
2.0	0.53 ± 0.01^{aB}	34.57	0.15 ± 0.01^{aA}	81.48	0.17 ± 0.01^{aA}	79.01	0.28 ± 0.01^{aB}	65.43	0.09 ± 0.01^{aA}	88.89	0.13 ± 0.01^{aB}	83.95

	Orange peel	Banana peel	Leave of date trees			
Mean of materials	0.49 ± 0.03^{C}	0.29 ± 0.01^{B}	0.25 ± 0.03^{A}			
Mean of treatment	KOH	H_3PO_4				
	0.36 ± 0.03^{B}	0.33 ± 0.02^{A}				
Mean of dose	0	0.4	0.8	1.2	1.6	2.0
	0.81 ± 0.01^{F}	0.47 ± 0.04^{E}	0.42 ± 0.03^{D}	0.32 ± 0.04^{C}	0.28 ± 0.04^{B}	0.22 ± 0.04^{A}

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

A, B & C: There is no significant difference (P>0.05) between any two means for the same attribute, within the same row have the same superscript letter.

Table (9): Effect of active carbons from different agricultural food wastes on the removal of heavy metal (Co^{+2}) ion from industrial wastewater before treatment

Dose (g)	Orange peel				Banana peel				Leave of date trees			
	KOH		H_3PO_4		KOH		H_3PO_4		KOH		H_3PO_4	
	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %
0	0.85 $\pm0.01^{eA}$	0.00	0.85 $\pm0.01^{fA}$	0.00	0.85 $\pm0.01^{fA}$	0.00	0.85 $\pm0.01^{fA}$	0.00	0.85 $\pm0.01^{fA}$	0.00	0.85 $\pm0.01^{eA}$	0.00
0.4	0.73 $\pm0.01^{dB}$	15.29	0.47 $\pm0.01^{eA}$	23.53	0.34 $\pm0.00^{eA}$	18.82	0.37 $\pm0.00^{eB}$	16.47	0.33 $\pm0.01^{eA}$	41.18	0.61 $\pm0.00^{dB}$	5.88
0.8	0.72 $\pm0.01^{dB}$	28.24	0.41 $\pm0.01^{dA}$	77.65	0.31 $\pm0.00^{dA}$	42.35	0.40 $\pm0.00^{dB}$	24.71	0.29 $\pm0.01^{dA}$	55.29	0.38 $\pm0.00^{cB}$	11.76
1.2	0.63 $\pm0.01^{cB}$	35.29	0.36 $\pm0.02^{cA}$	83.53	0.23 $\pm0.01^{cA}$	55.29	0.34 $\pm0.01^{cB}$	43.53	0.19 $\pm0.00^{cA}$	80.00	0.21 $\pm0.01^{bB}$	30.59
1.6	0.59 $\pm0.00^{bB}$	38.82	0.29 $\pm0.01^{bA}$	88.24	0.20 $\pm0.00^{bA}$	62.35	0.31 $\pm0.01^{bB}$	54.12	0.11 $\pm0.01^{bA}$	92.94	0.20 $\pm0.00^{bB}$	47.06
2.0	0.53 $\pm0.01^{aB}$	44.71	0.15 $\pm0.01^{aA}$	76.47	0.17 $\pm0.01^{aA}$	76.47	0.28 $\pm0.01^{aB}$	56.47	0.09 $\pm0.01^{aA}$	96.47	0.13 $\pm0.01^{aB}$	51.76

Mean of materials	Orange peel	Banana peel	Leave of date trees
	0.49 ± 0.03^{C}	0.29 ± 0.01^{A}	0.34 ± 0.03^{B}

Mean of treatment	KOH	H_3PO_4
	0.40±0.03A	0.46±0.03B

Mean of dose	0	0.4	0.8	1.2	1.6	2.0
	0.85 $\pm0.01^{F}$	0.68 $\pm0.02^{E}$	0.51 $\pm0.05^{D}$	0.38 $\pm0.04^{C}$	0.31 $\pm0.04^{B}$	0.28 $\pm0.04^{A}$

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

Table (10) Effect of active carbons from different agricultural food wastes on the removal heavy metal (Ni^{+2}) ion from industrial wastewater after treatment

	Orange peel				Banana peel				Leave of date trees			
	KOH		H_3PO_4		KOH		H_3PO_4		KOH		H_3PO_4	
	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %
0	1.81 ± 0.01^{fA}	0.00	1.81 ± 0.01^{fA}	0.00	1.81 ± 0.01^{fA}	0.00	1.81 ± 0.01^{fA}	0.00	1.81 ± 0.01^{fA}	0.00	1.81 ± 0.01^{fA}	0.00
0.4	1.74 ± 0.01^{eA}	3.87	1.80 ± 0.00^{eB}	0.55	1.72 ± 0.01^{eA}	4.97	1.74 ± 0.01^{eB}	3.87	1.74 ± 0.01^{eA}	3.87	1.73 ± 0.01^{eA}	4.42
0.8	1.70 ± 0.00^{dA}	6.08	1.74 ± 0.01^{dB}	3.87	1.65 ± 0.01^{dA}	8.84	1.70 ± 0.00^{dB}	6.08	1.70 ± 0.00^{dB}	6.08	1.68 ± 0.01^{dA}	7.18
1.2	1.58 ± 0.01^{cA}	12.71	1.70 ± 0.00^{cB}	6.08	1.42 ± 0.01^{cA}	21.55	1.65 ± 0.01^{cB}	8.84	1.60 ± 0.00^{cB}	11.60	1.42 ± 0.01^{cA}	21.55
1.6	1.32 ± 0.01^{bA}	27.07	1.51 ± 0.00^{bB}	16.57	1.27 ± 0.01^{bA}	29.83	1.47 ± 0.01^{bB}	18.78	1.47 ± 0.01^{bB}	18.78	1.30 ± 0.01^{bA}	28.18
2.0	0.94 ± 0.01^{aA}	48.07	1.18 ± 0.00^{aB}	34.81	0.88 ± 0.01^{aA}	51.38	1.02 ± 0.00^{aB}	43.65	1.02 ± 0.00^{aB}	43.65	0.99 ± 0.00^{aA}	45.30

Mean of materials	Orange peel		Banana peel		Leave of date trees	
	1.52 ± 0.05^{B}		1.45 ± 0.05^{A}		1.44 ± 0.07^{A}	
Mean of treatment	KOH		H_3PO_4			
	1.38 ± 0.05^{A}		1.51 ± 0.04^{B}			
Mean of dose	0	0.4	0.8	1.2	1.6	2.0
	1.81 ± 0.01^{E}	1.74 ± 0.01^{D}	1.69 ± 0.01^{C}	1.39 ± 0.09^{B}	1.39 ± 0.02^{B}	1.00 ± 0.02^{A}

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

Table (11): Effect of active carbons from different agricultural food wastes on the removal of heavy metal (Zn^{+2}) ion from industrial wastewater after treatment

Dose (g)	Orange peel				Banana peel				Leave of date trees			
	KOH		H_3PO_4		KOH		H_3PO_4		KOH		H_3PO_4	
	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %
0	0.19 ± 0.01^{dA}	0.00	0.19 ± 0.01^{fA}	0.00	0.19 ± 0.01^{fA}	0.00	0.19 ± 0.01^{fA}	0.00	0.19 ± 0.01^{fA}	0.00	0.19 ± 0.01^{dA}	0.00
0.4	0.14 ± 0.00^{cA}	26.32	0.16 ± 0.01^{eB}	15.79	0.15 ± 0.00^{eA}	21.05	0.17 ± 0.00^{eB}	10.53	0.17 ± 0.00^{eA}	10.53	0.17 ± 0.01^{dA}	10.53
0.8	0.13 ± 0.00^{cA}	31.58	0.13 ± 0.01^{dA}	31.58	0.13 ± 0.00^{dA}	31.58	0.14 ± 0.01^{dA}	26.32	0.14 ± 0.01^{dA}	26.32	0.14 ± 0.00^{cA}	26.32
1.2	0.08 ± 0.00^{bB}	57.89	0.06 ± 0.00^{cA}	68.42	0.08 ± 0.00^{cA}	57.89	0.10 ± 0.00^{cB}	47.37	0.10 ± 0.00^{cA}	47.37	0.10 ± 0.00^{bA}	47.37
1.6	0.08 ± 0.06^{bB}	57.89	0.03 ± 0.00^{bA}	84.21	0.03 ± 0.00^{bA}	84.21	0.05 ± 0.00^{bB}	73.68	0.05 ± 0.00^{bB}	73.68	0.03 ± 0.01^{aA}	84.21
2.0	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0 ± 0^{aA}	100.00	0.02 ± 0.00^{aB}	89.47
		Mean of materials			Orange peel		Banana peel		Leave of date trees			
					0.08 ± 0.01^{A}		0.08 ± 0.01^{A}		0.09 ± 0.01^{A}			
		Mean of treatment			KOH		H_3PO_4					
					0.08 ± 0.01^{A}		0.08 ± 0.01^{A}					
					0	0.4	0.8	1.2	1.6	2.0		
		Mean of dose			0.19 ± 0.01^{F}	0.16 ± 0.00^{E}	0.13 ± 0.00^{D}	0.08 ± 0.00^{C}	0.04 ± 0.01^{B}	0 ± 0^{A}		

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

Table (12): Effect of active carbons from different agricultural food wastes on the removal of heavy metal (Pb^{+2}) ion from industrial wastewater after treatment

Dose (g)	Orange peel				Banana peel				Leave of date trees			
	KOH		H_3PO_4									
	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %
0	0.72 $\pm0.01^{fA}$	0.00	0.72 $\pm0.01^{fA}$	0.00	0.72 $\pm0.01^{fA}$	0.00	0.72 $\pm0.01^{fA}$	0.00	0.72 $\pm0.01^{fA}$	0.00	0.72 $\pm0.01^{fA}$	0.00
0.4	0.67 $\pm0.01^{eB}$	6.94	0.47 $\pm0.01^{eA}$	34.72	0.70 $\pm0.00^{eB}$	2.78	0.46 $\pm0.01^{eA}$	36.11	0.46 $\pm0.01^{eA}$	36.11	0.47 $\pm0.01^{eA}$	34.72
0.8	0.59 $\pm0.01^{dB}$	18.06	0.40 $\pm0.01^{dA}$	44.44	0.46 $\pm0.01^{dB}$	36.11	0.41 $\pm0.01^{dA}$	43.06	0.41 $\pm0.01^{dA}$	43.06	0.42 $\pm0.01^{dA}$	41.67
1.2	0.54 $\pm0.01^{cB}$	25.00	0.32 $\pm0.01^{cA}$	55.56	0.40 $\pm0.00^{cB}$	44.44	0.25 $\pm0.01^{cA}$	65.28	0.25 $\pm0.01^{cA}$	65.28	0.32 $\pm0.01^{cB}$	55.56
1.6	0.44 $\pm0.01^{bB}$	38.89	0.19 $\pm0.01^{bA}$	73.61	0.29 $\pm0.01^{bB}$	59.72	0.17 $\pm0.01^{bA}$	76.39	0.17 $\pm0.01^{bA}$	76.39	0.21 $\pm0.01^{bB}$	70.83
2.0	0.15 $\pm0.01^{aB}$	79.17	0.08 $\pm0.01^{aA}$	88.89	0.09 $\pm0.01^{aA}$	87.50	0.08 $\pm0.01^{aA}$	88.89	0.08 $\pm0.01^{aA}$	88.89	0.10 $\pm0.01^{aB}$	86.11
		Mean of materials			Orange peel		Banana peel		Leave of date trees			
					0.38 ± 0.03^{C}		0.33 ± 0.03^{B}		0.29 ± 0.03^{A}			
		Mean of treatment			KOH		H_3PO_4					
					0.38 ± 0.03^{B}		0.29 ± 0.02^{A}					
		Mean of dose			0	0.4	0.8	1.2	1.6	2.0		
					0.72 $\pm0.01^{F}$	0.54 $\pm0.03^{E}$	0.45 $\pm0.02^{D}$	0.35 $\pm0.02^{C}$	0.24 $\pm0.02^{B}$	0.10 $\pm0.01^{A}$		

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

Table (13): Effect of active carbons from different agricultural food wastes on the removal of heavy metal (Co^{+2}) ion from industrial wastewater after treatment

Dose (g)	Orange peel				Banana peel				Leave of date trees			
	KOH		H_3PO_4		KOH		H_3PO_4		KOH		H_3PO_4	
	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal %	Amount mg/L	Removal ion %	Amount mg/L	Removal %	Amount mg/L	Removal %
0	0.80 $\pm0.01^{fA}$	0.00	0.80 $\pm0.01^{fA}$	0.00	0.80 $\pm0.01^{fA}$	0.00	0.80 $\pm0.01^{fA}$	0.00	0.80 $\pm0.01^{fA}$	0.00	0.80 $\pm0.01^{fA}$	0.00
0.4	0.51 $\pm0.01^{eB}$	36.25	0.54 $\pm0.01^{eA}$	32.50	0.65 $\pm0.01^{eA}$	18.75	0.69 $\pm0.01^{eB}$	13.75	0.69 $\pm0.01^{eB}$	13.75	0.59 $\pm0.01^{eA}$	26.25
0.8	0.48 $\pm0.00^{dB}$	40.00	0.19 $\pm0.01^{dA}$	76.25	0.60 $\pm0.00^{dA}$	25.00	0.66 $\pm0.00^{dB}$	17.50	0.66 $\pm0.00^{dB}$	17.50	0.55 $\pm0.00^{dA}$	31.25
1.2	0.40 $\pm0.00^{cB}$	50.00	0.14 $\pm0.01^{cA}$	82.50	0.50 $\pm0.01^{cA}$	37.50	0.60 $\pm0.00^{cB}$	25.00	0.60 $\pm0.00^{cB}$	25.00	0.34 $\pm0.01^{cA}$	57.50
1.6	0.34 $\pm0.01^{bB}$	57.50	0.08 $\pm0.00^{bA}$	90.00	0.45 $\pm0.01^{bA}$	43.75	0.48 $\pm0.00^{bB}$	40.00	0.48 $\pm0.00^{bB}$	40.00	0.31 $\pm0.01^{bA}$	61.25
2.0	0.23 $\pm0.01^{aB}$	71.25	0.05 $\pm0.00^{aA}$	93.75	0.31 $\pm0.00^{aA}$	61.25	0.34 $\pm0.01^{aB}$	57.50	0.34 $\pm0.01^{aB}$	57.50	0.25 $\pm0.01^{aA}$	68.75
	Mean of materials				Orange peel		Banana peel		Leave of date trees			
					0.29 ± 0.03^{A}		0.53 ± 0.02^{B}		0.48 ± 0.03^{C}			
	Mean of treatment				KOH		H_3PO_4					
					0.48 ± 0.02^{B}		0.39 ± 0.03^{A}					
	Mean of dose				0	0.4	0.8	1.2	1.6	2.0		
						0.61 $\pm0.02^{E}$	0.52 $\pm0.04^{D}$	0.43 $\pm0.04^{C}$	0.35 $\pm0.03^{B}$	0.25 $\pm0.02^{A}$		

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

The removal of cobalt (Co^{+2}) was found to 57.50% for leaves of date trees, but for banana peel, the value was significantly higher where they have been found to be (61.25%) at same maximum dose (2.0g). However, the highest level of removal percentage of Co^{+2}observed in the case of active carbons produced from orange peel by activation method with KOH which was 71.25% at the same dose (2.0g) of bioadsorbent. The accomplished results are slightly different with those reported by **Abbasi *et al.*, (2013).**

Conclusion

From the above-mentioned results, it can be concluded that the orange peel, banana peel and leave of date trees, like most other natural absorbents can be used in the treatment process for removal of metals induced heavy metals such as nickel (Ni^{+2}), copper (Cu^{+2}), zinc (Zn^{+2}), lead (pb^{+2}), cobalt (CO^{+2}) and cadmium (Cd^{+2}). The treatment efficiency may be as reached reached to 100% by choosing the adsorbent amount precisely. Finally, the residues of food wastes can be processed and converted to be adsorbents this is due to theis large surface areas, cheap high swelling capacities, excellent mechanical strengths, and are convenient to use for removal heavy metalsof wastewater.

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إزالة أيونات المعادن الثقيلة من مياة الصرف الصناعي بإستخدام المخلفات الزراعية المختلفة

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الملخص العربي

يعتبر تلوث المياة من أهم المشاكل التي تسبب الكثير من الأمراض فأغلب المخلفات الصناعية تصرف في النيل دون معالجة مما يسبب تلوث كيميائي وبيولوجي لهذه المياة وكذلك تؤدي الي زياده نسبة العناصر الثقيلة بها. لذلك فإن الهدف من هذه الدراسة معالجة مياة الصرف الصناعي بمنطقة مبارك الصناعية بقويسنا حيث أن مياة الصرف الناتجة من هذه المصانع تحتوي علي تركيزات عالية من بعض المعادن بما فيها المعادن الثقيلة مثل (النيكل, النحاس ,الزنك , الرصاص , الكوبالت , الكادميوم) والوصول بتركيزات هذه العناصر الى الحدود الآمنة والمسموح بها في القانون رقم ٤ لسنة ١٩٩٥ م وتعديلاتة وذلك بإستخدام الكربون النشط المحضر بإستخدام بعض المخلفات الغذائية مثل قشور البرتقال , قشور الموز وأوراق أشجار النخيل بهدف الإستفادة من المياة المعالجة بجانب تحويل المخلف الزراعي الي مادة مفيدة وتقليل التلوث البيئي.

ومن النتائج المذكوره أعلاه, يتضح أن قشور البرتقال وقشور الموز و أوراق أشجار النخيل من المواد التي لها القدرة على عملية إدمصاص المعادن بما فيها المعادن الثقيلة من النيكل والنحاس والزنك والرصاص والكوبالت والكادميوم والتي يمكن إستخدامها في عمليات المعالجة وذلك بإنتاج الكربون النشط بطريقتي التنشيط بواسطة (١٠%) هيدروكسيد البوتاسيوم , (١٠%) من حامض الفوسفوريك حيث تم دراسة تأثير إستخدام تركيزات مختلفة (٠.٤ , ٠.٨ , ١.٢ , ١.٦ , ٢ جم) من الكربون النشط المحضر من المخلفات الغذائية , وقد تصل نسبة الإدمصاص الى ١٠٠% وذلك لكفائتها العالية وسهولة إستخدامها ورخص ثمنها.