The use of natural materials as adsorbents and color removal of municipal wastewater

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Abstract

The activated carbon from seeds of dates was prepared by four methods: acid-treated, base-treated, steam-treated and heat-treated. All were compared with commercial activated carbon. The steam treated activated carbon has the highest surface area, and electrical conductivity, also the highest removal efficiency of Chemical oxygen demands (CODs) particles.

Freundlich adsorption isotherms was used to analyze the adsorption efficiencies and the steam-treated carbon showed a higher adsorption capacity comparing to the commercial activated carbon.

There is a great commercial potential to use dates' seeds since they may be provide renewable raw materials that found in great abundance and the use of them to offer solution to the environmental problems and help the agricultural economy with an additional market potential.

Keywords: activated carbon, dates, COD, refining, municipal drinking wastewater filtration, activated carbon, Freundlich model.

Introduction

The increase in population and the rising standard of living lead to a rising demand for fresh wastewater. Iraqi refining plants face so many problems, most importantly the decrease in electricity and the old age of many stations. Even with several environmental laws, many industries discharge untreated or inadequately treated wastewater into Tigris or Euphrates rivers. Albu-Etha (Al-Karkh, Baghdad) sewage wastewater plant has a capacity of 205,000 $m^3.d^{-1}$, while it received 625,000 $m^3.d^{-1}$, while al-Rustamia plant (Rusafa, Baghdad) has a capacity of 175,000 $m^3.d^{-1}$, and received 250,000 $m^3.d^{-1}$ (Ministry of Industry, Special Report on wastewater plants of Iraq, 2010).

Iraqi people, epically middle-class families are concerned about the safety of their drinking wastewater, especially where the wastewater is supplied in old iron pipes systems, where lead is used for soldering faucets and other connections. The leaching of lead from these lead-based solders is thought to be one of the major causes for the occasional findings of lead in drinking wastewater. Lead heads the list of environmental threats because, even at extremely low concentrations, lead has been shown to cause brain damage in children (Barbosa et al, 2005, Patrick, 2006, Guidotti and Ragain , 2007). This led to the use of bottled refining for drinking and most houses planted a variety of wastewater treatment devises that used filter systems with ion exchange resin or activated carbon, but these systems have been shown to be ineffective in removing all known hazardous contaminants. Still, the families are forced to use piped wastewater for washing and cooking. (WHO Bulletin, 2011; WHO reports, 2008, 2010, 2011)

Additionally, many tap wastewater sources, especially in remote rural areas, have undesirable and sometimes harmful color, odor, and hardness (from high zinc concentrations) that prompt consumers to seek ways to improve their tap wastewater quality in their homes by various filtration devices.

Granular activated carbon is an adsorbent with wide range of applications. It most effective adsorbents in food industry, mineral industry, and also used in sugar refining, chemical, pharmaceutical industries, but is commonly used for recycling municipal and industrial wastewater as an adsorbent. The cost of treatment of municipal wastewater counts for 25-65% operational cost, so many researchers were encouraged to find an alternative (Amuda and Ibrahim, 2006).

Commercially activated carbon is produced from bituminous or lignite coal, but it can be prepared from a large variety of carbon-containing feedstock by pyrolysis into char and subsequent physical or chemical activation of the char. Almost all agricultural by products such as coconut shells (Tam et al., 1999, Amuda and Ibrahim, 2006), wood, bone, peat processed bagasse (Ahmedna, et al , 2000) scrap tires and saw dust (Hamadi et al, 2001), pistachio (Wartelle and Marshall , 2001) , rice products (Yalem and Sevine, 2000), Akhtar et al , 2005), sugarcane (Girigis et al., 1994, Ahmedna et al., 2000) and biomass such as *Aspergillus tereus* (Azab and Peterson, 1989), *Pseudomonas* sp. (Husseein et al., 2004), *Rhizopus arrhizus* (Preetha and Viruthagiri, 2005) have been reported to be important adsorbents for the removal of metals and organics from municipal and industrial wastewater.

The author, in the present study seeks a low cost technology that can replaced the activated carbon as an adsorbent by processing seeds of dates (***Phoenix dactylifera***) into granulated activated carbon. The objective of the study is to evaluate the use of the activated carbon produced from seeds of dates in the filtration system to determine its effectiveness in removing contamination and compared the adsorption efficiency of seeds of dates based-activated carbon with that of commercial activated carbon for removal of pollutant organic materials from wastewater.

Materials and methods

Materials

10L of crude river wastewater were collected from old Rustmia plant, Rusafa, Baghdad and filtered using Whatman No. 1 filter paper to remove suspended solids particles and used immediately. Activated carbon was purchased from BDH chemicals. Dates fruits were obtained from local markets. All reagents used were of analytical grade. 3g carbon were used per 100mL of wastewater.

Methods

Preparation of seeds

Seeds from dates were washed with distilled water twice to remove dusts , dried in room temperature, pulverized and sieved to 2-3 mm particle size. The pulverized seeds were pyrolyzed in a furnace at 600°C for 2h and then washed again with distilled wastewater to remove all contaminants. After drying at room temperature, the pyrolyzed seeds were crushed into powder form and then divided into four batches that were treated (each) by a different method.

Acid treatment

0.05M nitric acid was added to the first batch (3:1 v/w) and left in an oven at 110°C for 24h and then soaked in distilled wastewater for 6h, followed by soaking in 2% $NaHCO_3$ until all acid residues were removed. It was dried at 110°C for 24h and used as a (acid-treated).

Base treatment

0.05M sodium hydroxide was added to the second batch (3:1 v/w) and left in an oven at 110°C for 24h and then soaked in distilled wastewater for 6h, followed by soaking in 2% HCl until all base residues were removed. It was dried at 110°C for 24h and used as a (base-treated).

Steam treatment

The third batch was dipped in 5% sodium chloride for 48h and dried slowly through an oven. The batch was steamed through autoclaved for 6h at 600°C and was dried at room temperature. The dried carbon was washed with 0.05M HCl four times to remove all water impurities and then dried in an oven at 200°C for 48h and used as (steam-treated).

Heat treatment

The fourth batch was placed in a stainless steel container in an oven at 900°C for 6h and then left to cool at room temperature and used as (heat-treated).

COD measurement

Chemical Oxygen Demand (COD) is defined as the quantity of a specified oxidant that reacts with a sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. COD is expressed in mg/L 0_2.

The COD is measured as a rapid indicator of organic pollutant in wastewater. It is normally measured in both municipal and industrial wastewater treatment plants and gives an indication of the efficiency of the treatment process. The efficiency of the treatment process is normally expressed as COD removal, measured as a percentage of the organic matter purified during the cycle.

The US Environmental Protection Agency specifies that the only acceptable reportable measuring method for COD is the colorimetric dichromate method (Jirka and Carter, 1975). Advantages in using this method include high accuracy, certifiable results and abate chloride interference. The COD is heated to 150ºC (±2ºC) for 2 hours to ensure accurate pre-heating and then the sample is refluxed in strongly acidic solution with a known excess of potassium dichromate ($K_2Cr_20_7$). After digestion the remaining unreduced $K_2Cr_20_7$ is titrated with ferrous ammonium sulphate to determine the amount of $K_2Cr_20_7$ consumed and the oxidisable matter is calculated in terms of oxygen equivalent. When a sample is digested, COD material in that sample is oxidized by the dichromate ion. The result is the change in chromium from the hexavalent (VI) to the trivalent (III) state. Both chromium species exhibit a color and absorb light in the visible region of the spectrum. All concentrations of COD were measured at 560nm

In order to calculate the removal efficiency rate of COD (E%), the following equation was set:

$E (\%) = [C^1-C^2/C^1] \times 100$

where: C^1 and C^2 are the initial untreated and equilibrium concentration of COD ($mg.L^{-1}$), respectively.

The initial concentration of COD was determined colorimetrically

Freundlich adsorption isotherm

Freundlich adsorption isotherms were performed in a set of plastic centrifuge tubes (50mL), where solutions of COD with different initial concentrations were placed. The tubes were placed on a shaker and stirred for a certain time according to the method of Yan Pan et al (2000) according to the following equation:

$\text{Log } q = \log K + 1/n \log p$

$\text{Log } (x/m) = \log K + (1/n) \log p$

where $n > 1$.

K is a temperature-dependent constant.

X= mass of adsorbate, m= mass of adsorbent

p= equilibrium concentration of adsorbate (COD) in solution

At high pressure $1/n = 0$ Hence extent of adsorption is independent of pressure

The plot of log q vs. log p gives a straight line with slope of (1/n) and y-intercept of log K

Other methods

Density was measured by Pentapyc 5200e & Ultrapyc 1200e (Quantachrome Instruments, USA). pH was measured by HI 2212 pH Benchtop Meter with Three Point Calibration (Hanna instruments, USA). Conductivity was measured by Portable Conductivity/ TDS Meters (HANNA instruments, USA). Surface area, pore size distribution and total pore volume were measured by Micromeritics Tristar II 3020 Surface Area Analyzer (Porous Materials Inc., USA).

Carbon dosages ranging from 0 to 3 g per 100 mL of municipal wastewater were used for adsorption. The reaction mixture was agitated at 150 rpm using a Teflon coated half-inch bar on a Corning magnetic stirrer for 2 h to ensure equilibrium. After this period of adsorption, the sample was filtered using Whatman no.1 filter paper, and the filtrates were analyzed for residual COD in the wastewater using colorimetric method (5220D) recommended by the Standard Method for Examination of wastewater (AWWA, 1991).

Results

Characterizations of the activated carbon

The activated carbons characteristics (surface area, density, pH, conductivity, hardness and color removal) as can be seen in Table 1.

The commercial carbon was used as a control in order to judge the characteristics of the activated carbon produced from seeds of the dates.

From Table 1, all batches treated (except heat-treated batch) showed physical characteristics close to those of the commercial activated carbon.

Steam-treated gave the highest surface area of 520nm^2 followed by acid-treated with 5003nm^2,and then base-treated (481nm^2) whereas the commercial carbon has a surface area of 510nm^2.

The density of acid-treated (0.88g.cm^{-3}) was higher than the densities of base-treated (0.81g.cm^{-3}), and steam-treated (0.82g.cm^{-3}), while the commercial activated charcoal (0.90g.cm^{-3}).

The steam-treated displayed a higher electrical conductivity (5.0×10^{-6} p(Ω·m)), followed by acid-treated (4.80 ×10^{-6} p(Ω·m)), base-treated (4.10×10^{-6} p(Ω·m)), while commercial activated carbon has a conductivity of treated (4.80×10^{-6} p(Ω·m)).

All activated carbons obtained from the seeds of dates have a pH in the range of 6.7-7.0, and all has the ability to remove color efficiently as the commercial charcoal.

Hardness ranged between 62-68%, while the commercial carbon has hardness 0f 76%.

The heat-treated seeds gave the lowest results in all treatments.

Table 1.characterizations of dates based activated carbon and commercial

activated carbon

Characteristics	**Activated carbon (from seeds of dates)**				**Commercial activated carbon**
	Acid-treated	**Base-treated**	**Steam-treated**	**Heat-treated**	
Surface area (nm^2)	503	481	520	320	510
Density ($g.cm^{-3}$)	0.88	0.81	0.82	0.34	0.90
pH	6.8	6.7	7.0	4.0	7.20
Conductivity p(Ω·m)	4.80×10^{-6}	4.10×10^{-6}	5.0×10^{-6}	3.80×10^{-6}	4.80×10^{-6}
Color removal	+++	+++	+++	+	+++
Hardness	65.1	62.3	67.7	29.3	76.9

Removal efficiency of COD

The COD has an initial concentration of about 2435 mg/L with an average pH of 7.0. The dosage of carbons employed for adsorption ranged from 0.0 to 10.0 g of carbon/100 mL of municipal wastewater.

The removal efficiency of the activated carbon increased with the increased dose. The steam treated carbon showed the highest removal efficiency of COD followed closely by acid-treated and commercial carbon.

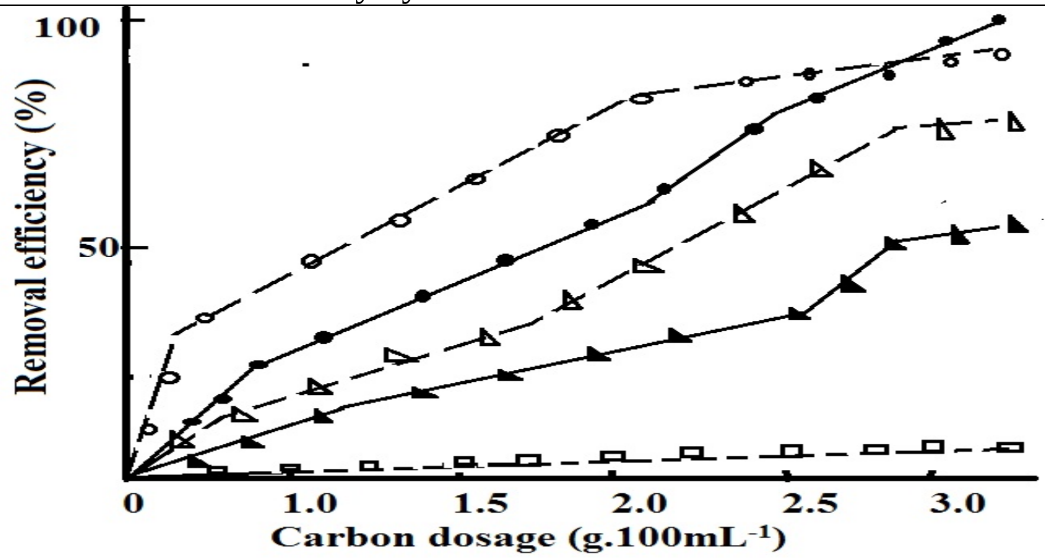

Fig.1. The efficient removal of COD by the five types of activated carbons. Steam treated (o), acid-treated (Δ), base-treated (▲), heat-treated (□) and commercial activated carbon (●).

Adsorption isotherm

Freundlich adsorption isotherm was measured the relation between the concentration of organic matters (expressed as COD) adsorbed by activated carbon and COD equilibrium concentration in wastewater. The heat of adsorption is many instances decreases in magnitude with increasing extent of adsorption. This decline in heat of adsorption is logarithmic, implying that adsorption sites are distributed exponentially with respect to adsorption energy.

From Fig. 2, the equilibrium data has a very high correlation coefficients value (about 0.9) for all carbons (except heat-treated) which confirms the applicability of Freundlich isotherms.

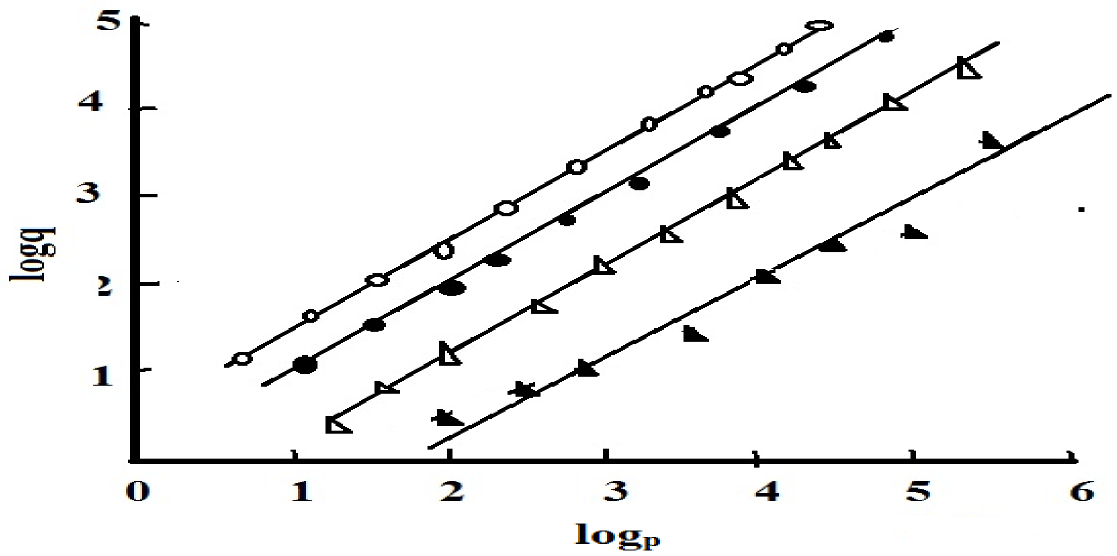

Fig.2. Freundlich plots for the COD adsorption onto the activated carbon. Steam treated (o), acid-treated (Δ), base-treated (▲), and commercial activated carbon (●).

Loq q values represent the relative adsorption efficiency of the activated carbon, while logp represents the residual concentration of COD in the treated municipal wastewaters.

A larger value of K indicates good adsorption efficiency for an activated carbon, while large value of 1/n indicates a large change in effectiveness over different equilibrium concentrations. The equilibrium data in Freundlich adsorption isotherm is shown in Table 2

Table 2. The equilibrium data of Freundlich adsorption isotherms

Activated carbon	K	1/n	Correlation coefficient
Acid-treated	150.8	0.45	0.855
base-treated	100.90	0.42	0.861
Steam-treated	116.5	0.49	0.873
Heat-treated	70.3	0.65	0.851
commercial activated carbon	120.10	0.72	0.873

The cost

The cost of producing activated charcoal from the seeds of the dates is very important. As can be shown in Table 3, the estimated cost consists of raw material costs (dates), carbon production costs and miscellaneous is $5.o5.

Table 3. The estimated cost of activated charcoal produced from the seeds of dates

Item	**Cost ($ per Kg of carbon)**
dates	0.50

Activated carbon production	4.0
Miscellaneous costs	0.55
Total cost	5.05
Cost of commercial carbon	7.0

Discussion

The steam-treated activated carbon from seeds of dates recorded the highest removal efficiency of organic matter expressed as COD, than acid and base-treated activated carbon. This is excepted due to the fact that adsorption of the organic matter in the wastewater is a function of carbon surface area (Firoozian et al, 2011; Tan et al, 2008)

Of course, high surface area may allow increased adsorption of metal ions if the internal carbon surfaces can accommodate some adsorption of the positively charged metals (Firoozian et al, 2011)

The densities are within the limit of the standards of The American water work Association (0.7-1.0) which has set a lower limit on bulk density at 0.25gm/ml for activated carbon to be of practical use (AWWA, 1991)

The electrical conductivity test is important because it shows the presence of leach able ash which is considered impurity and undesirable in activated carbon. The activated carbon from dates low conductivity values which indicate that an acid or steam-treated wash was enough to reduce leach able ash to levels observed in commercial carbon. The results of electrical conductivity indicated that all amounts of wastewater soluble materials (such as silica, aluminum, iron, magnesium, and calcium) in the treated carbon were removed and the obtained carbon has purity so it can be used for commercial decolorization.

An activated carbon should possess sufficient mechanical strength to withstand the abrasion resulting from continued use to minimize attrition, especially carbon used for decolorization since in the course of carbon usage particle may breakdown and dust formation occur. It showed no breakage during color decolorization.

Most activated carbon produced from plants will have ash leached into the liquid during the process of decolorization which will interfere with carbon adsorption through competitive adsorption and catalysis of adverse reactions. And lead to low surface area. The ash content may affect the pH of the carbon since the pH of most commercial carbons is produced by their inorganic components. Usually materials with the lowest ash content produce the most active products.

The American water work Association has set the standards of pH between 6- 7 for activated carbon to be of practical use (AWWA, 1991). All activated carbon produced, except heat treated, were within this range. Activated carbon pH may influence color by changing the pH of the wastewater. Acid-treated carbons for example may be a better decolorizer but technicians in wastewater refinery would seldom employ a highly acidic carbon because the acid would cause unwanted results. The same can be said about base-treated carbon. Hence a carbon pH of 6-8 is acceptable for most application.

Steam treated showed the best potential for producing activated carbon with both satisfactory physical and chemical Properties making it a good candidate for wastewater decolorizer.

The steam-treated has the highest value of k indicates a good adsorption efficiency for this particular activated carbon. It was about 50% more than the commercial carbon. The commercial carbon has a larger value of 1/n which indicates that it has the highest rate of adsorption of COD in wastewater, but its adsorption capacity for the organic materials is minimal.

The author estimated the total cost of producing activated charcoal from dates is about $5.05/1Kg of carbon, and this about $2 dollars less than the cost of the commercial carbon. Since 30% of dates harvested are wasted (Iraqi Ministry of Agriculture, 2010), so this can be used as a renewable source of specialty granular activated carbons. Activated carbon from dates can be used in sugar, soft-drinks, and leather industries, just to name few. This will help to reduce the cost of waste disposal and provide renewable materials that found in great abundance. More important, the raw materials do not have to be imported, and the use of dates offer solution to environmental problems and help the agricultural economy with an additional market potential.

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الملخص

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تم تحضير الكربون المنشط من نوى التمر من خلال أربعة طرق: معامل بالحامض، معامل بالقاعدة، معامل بالبخار، ومعامل بالحرارة، وتمت مقارنة بين الكربون الناتج والكربون المنشط التجاري، ووجد ان الكربون المنشط المعامل بالبخار لديه مساحة أوسع وقدرة أعلى على التوصيل الكهربائي، وأيضا كفاءة عالية لإزالة الجزيئات الكيمياوية القابلة للأكسدة COD.

تم استخدام امتزاز فروندليتش الحراري لتحليل الكفاءة الامتزازية للكربون، ووجد ان الكربون المعامل بالبخار لديه سعة امتزازية كبيرة مقارنة بالكربون المنشط التجاري.

هناك احتمال تجاري كبير لاستخدام نوى التمور لأنها يمكن أن توفر مواد خام متجددة موجودة في وفرة كبيرة والاستفادة منها لتقديم حل للمشاكل البيئية ومساعدة الاقتصاد الزراعي مع خلال اضافة إمكانات سوقية جديدة.