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Utilization of Agricultural Waste in Treating Water Pollutants

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Abstract

This study investigated the applicability of chemically (phosphoric acid) activated bagasse pith and date pits in the adsorption of water pollutants. The textural properties including porous parameters, monolayer equivalent surface area, total pore volumes, average pore radius, Methylene blue number and other physic-chemical characterization were investigated. The activated carbons were analyzed for moisture content, ash content. Ultimate analysis was done by using CHNS analyzer (Cairo University, Micro-analytical Center). To investigate the effect of phosphoric acid on the raw material, thermo gravimetric analysis (TGA) and differential thermo gravimetric (DTG) recordings were determined. The adsorption of heavy metals as pollutants, including Co, Sr, Cu, Cs, Pb, Cd, Ni, Fe, Zn, was studied in a batch experiments. Comparison of date pits activated carbon with commercial activated carbon was done, and the results indicated that using of prepared activated carbon for removal of Co, Sr, Cu, Cs, Pb, Cd, Ni, Fe, Zn was more effective than commercial activated carbon.

Keyword:- water pollutants; Textural properties; thermo gravimetric analysis; differential thermo gravimetric.

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Introduction

Activated carbons are the most popular adsorbents used for the removal of toxic substances from water. This could be related to their extended surface area, high adsorption capacity, micro porous structure and special surface reactivity [1]. However, the adsorptive capacity of activated carbons depends mainly on the precursor nature, the operating conditions of adsorption (such as temperature and pH) and the nature of the adsorbate. The carbon precursors may be of botanical origin (wood, coconut shells, fruit seeds), mineral origin (coal, peat), or polymeric materials (rubber, tires, plastics). About 50% of industrially available activated carbons are derived from precursors of botanical origin [2]. These precursors are usually low-cost agricultural by-products with no notable applications except as fuels for energy generation. Numerous agro-waste biomaterials have been used for the production of activated carbons, including coconut shells, almond shells, peach stones, apricot stones, plum stones, cherry stones, apple pulp, and nutshells [3]. Bagasse Pith (BP), and Date Pits (DP) have received less consideration as a source material for the preparation of activated carbon. Raw agricultural solid waste materials generally do have some adsorption capacity, but are greatly enhanced by the activation process. Activated carbon can be made from many substances containing high carbon content. The raw material has a very large influence on the characteristics and the performance of activated carbon. Activated carbons could be produced by either physical (thermal) activation or chemical activation. Thermal activation involves carbonization or calcinations of the raw materials at elevated temperatures (500-900^{0}C) in an inert atmosphere followed by mild oxidation (gasification) of the substance with steam, air and/or carbon dioxide at high temperatures (800-1000^{0}C). Simultaneous carbonization and activation can also be obtained chemically by impregnation with dehydrating agents such as phosphoric acid and zinc chloride [4]. This work presents results on the adsorption of water pollutants by chemically (phosphoric acid) activated date pits. For example, date pits constitute roughly 10% of the date palm [5]. Date pits (DP) as a waste stream have been a problem to the date industry, therefore, its recycling or re-utilization is useful. In the United States, pulverized ground date pits are being used on a small scale, on dirt roads as a type of road base gravel. In the Middle East, it is sometimes used in animal feed [6]. Therefore, finding ways to use this agricultural by-product profitably will benefit date farmers substantially and offers an interesting alternative for their disposal.

Experimental

Preparation of activated carbon

Date pits and Biogases pith were chosen as precursors for the production of activated carbons by one-step chemical activation using H_3PO_4 to study the effect of the precursor nature on the adsorptive capacity of activated carbons. In each experiment, 30 g of crushed precursor was soaked in 50 ml of 75 % H_3PO_4 solution to cover it completely, slightly agitated to ensure penetration of the acid throughout, then the mixture heated to 80°C for 1 h and left overnight at room temperature to help appropriate wetting and impregnation of the precursor [7]. The impregnated mass was dried in an air oven at 80°C overnight, then, admitted into the reactor (ignition tube), which was then placed in a tubular electric furnace open from both ends. The temperature was raised at the rate of (50°C/15 min.) to the required end temperature. The carbonization process was carried out at 550^{0}C for 100 min. The product was thoroughly washed with hot distilled water till pH = 6.5, and finally dried at 110°C.

Characterization of activated carbon

Particle size was determined using sieves of different particle size. Packed and apparent densities were determined by a tamping procedure using a 25 ml graduated glass cylinder [8]. The texture characteristics were determined by the standard n2 adsorption isotherms, followed by their analysis to evaluate the porous parameters. Nitrogen adsorption isotherms were conducted at liquid nitrogen temperature using a NOVA 1000 instrument (Chromatic). Thus, from the BET plots the "monolayer equivalent surface area" (Sbet) was obtained, the total pore volumes estimated from the volume of nitrogen adsorbed at p/p° = 0.95 (Vf) and an average pore radius from r = 2Vp/SBET. Methylene blue number was estimated by the extent of adsorption of milligrams of methylene blue adsorbed by 1 g of carbon in equilibrium with a solution of methylene blue having a concentration of 1.0 mg l-1. The activated carbon was analyzed for moisture content, ash content. Ultimate analysis was done by using CHNS analyzer (Cairo University, Micro-analytical Center).

Thermo gravimetric analysis:

In order to detect the effect of phosphoric acid on the raw material thermo gravimetric analysis (TGA) and differential thermo gravimetric (DTG) recordings were determined. The raw finely powdered raw materials and a sample impregnated with 75 vol. % H3PO4 (dried at 1050C) were analyzed in the micro analytical center, Cairo University. Thermal Analysis system was used at a heating rate of 100C min-1 up to 9000C.

Collection of water sample:

Sample number 1: is a ground water of 21 m depth, sample number 2: is a ground water of 66 m depth (from another site). Sample number 3: is a ground water of 12 m depth and sample number 4: is surface water. Water sample were collected by polyvinyl chloride bottle (5 L capacity) two meter depths at the selected points [9]. Water samples were kept into a one-litre polyethylene bottle in ice box and analyzed in the laboratory.

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Treatment of surface and ground water samples.

The collected water samples were treated using prepared activated carbon to investigate its efficiency. Weight of 0.2 gm of activated carbon was shacked with 20 ml of water sample for 2 hr, and then the samples were centrifugated for 5 minutes at 5000 rpm and the supernatant of each sample was analyzed using AAS.

Results and discussion

Analysis of the water samples

The water samples were analyzed for some metal ions which are commonly found in water and the results are summarized in the following Table(1)

Table 1. Analysis of sample water

Metals	Sample 1	Sample 2	Sample 3	Sample 4
Co	0.001	0.030	0.002	0.010
Sr	0.380	0.410	0.080	0.070
Cu	0.003	0.010	0.002	0.003
Cs	0.004	0.010	0.001	0.002
Pb	0.030	0.030	0.002	0.020
Cd	0.010	0.020	0.020	0.010
Ni	0.028	0.025	0.026	0.022
Fe	0.050	0.035	0.041	0.051
Zn	0.036	0.003	0.012	0.007
Cr	0.060	0.070	0.060	0.080

Characterization of prepared activated carbon:

- **Physico-chemical characterization:**

The following tables summarize some of the physic-chemical characterization of the prepared activated carbon.

- **Thermo gravimetric analysis:**

During the pyrolysis of lignocellulosic materials, three stages can be distinguished. These are: (a) loss of water in the 25-280 0C range, (b) primary pyrolysis in the 290-480 0C range with evolution of most gases and tars with formation of the basic structure of the char, and (c) consolidation of the char structure at 510-850 0C with a small weight loss [10]. Despite the influence of the intrinsic chemical composition (relative content of the constituents: cellulose, hemicelluloses and lignin), the extrinsic factor of the chemical impregnant would be equally effective in directing the course of pyrolysis. Thermo Gravimetric Analysis indicated the effect of phosphoric acid on the surface of DP activated carbon as shown in Fig (1).

Table (2): Characterization of DP activated carbon and its precursor material.

Porosity characteristics of DP activated carbon		Physicochemical analysis of DP activated carbon	
Specific surface area, S_{BET} (m^2g^{-1})	615	Methylene blue (mgg^{-1})	226
Average pore diameter (Å)	25.5	Acid solubility (%)	8
Total pore volume ($cc.g^{-1}$)	6.051	Base solubility (%)	11
Micropore volume ($cc.g^{-1}$)	0.136	Water solubility (%)	3
Micropore area ($m^2.g^{-1}$)	201.58	Moisture content (%)	3.1
External surface area ($m^2.g^{-1}$)	413.28	Apparent density ($g.cc^{-1}$)	0.381
		Packed density ($g.cc^{-1}$)	0.546
Chemical analysis of DP activated carbon		Chemical composition of DP raw material [10]. (Wt. %)	
C %	65.09	Moisture	8.0

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N %	1.30	Oil	8.8
Ash content	5.5	Protein	5.0
H %	3.16	Carbohydrates(cellulose, hemicellulose and lignin).	61.0
S %	0.87	Fibre	15.7
O % (by difference)	22.64	Inorganic percent	1.4

Table (3) :Physicochemical characterization of BP activated carbon.

Parameters	Values	Parameters	Values
Carbon yield (%)	93	Phenol number (mg)	159
Ash content (%)	6.2	Iodine number ($mg.g^{-1}$)	750
Methylene blue number ($mg.g^{-1}$)	285	Particle size (mm)	1.0 - 0.25
Packed density ($g.ml^{-1}$)	0.289	Matter soluble in water (%)	1.5
Apparent density($g.ml^{-1}$)	0.18	Matter soluble in acid (%)	2.2
BET surface area ($m^2.g^{-1}$)	530	Matter soluble in base (%)	2.1
Langmuir surface area ($m^2.g^{-1}$)	767	Moisture content (%)	5.5
Average pore radius (Å)	16.0	C %	77.76
Half pore width (Å)	8.365	H %	3.66
Micropore surface area ($m^2.g^{-1}$)	620.6	N %	2.4
Total pore volume ($cm^3.g^{-1}$)	0.405	S %	0.5
Micropore volume ($cm^3.g^{-1}$)	0.099	O % (by difference)	14.88
Mesopores volume ($cm^3.g^{-1}$)	0.304	pH	3.3
Point of zero charge (pH_{PZC})	4.2		
Chemical analysis of BP raw material %			
α-Cellulose	53.7	Alcohol/benzene solubility	7.5
Pentosan	27.9	Ash	6.6
Lignin	20.2		

According to Figure (1), raw date pits (DP) exhibit only one prominent wave of weight loss (between 220 and 350 0C) with a maximum centered at 260 0C, followed by a slow weight loss with decreasing rate. A considerably different pattern is exhibited by the H3PO4-treated lignocellulosic material (HDP).

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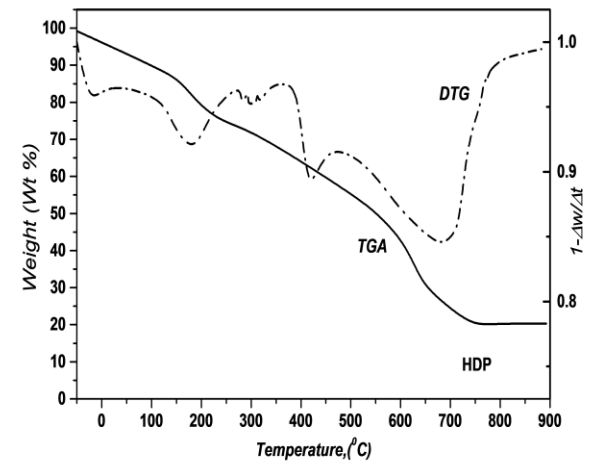

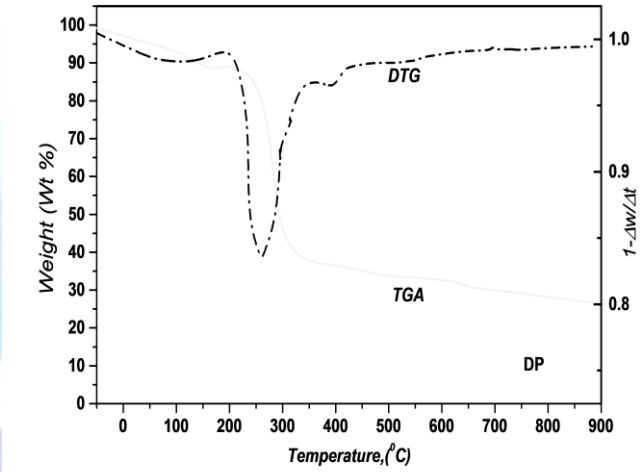

Figure (1): TGA and DTG for date pits (DP) and 75% H_3PO_4-impregnated date pits (HDP).

Scanning electron microscope.

The surface topography of activated carbon samples and analysis of adsorbed metal were examined using SEM. Figure 2 show the SEM photograph of the activated carbon obtained from DP. Carbonization and activation of DP result in porous with a considerable surface area. The DP pyrolysis occurs rapidly with gas evolution at a higher temperature, thus destroying partially the original DP structure [11]. On the other hand, volatiles are gradually released at a lower and wider temperature range. Thus, the sample consists of particles that are partly porous, as shown in the SEM photographs of Figure 2.

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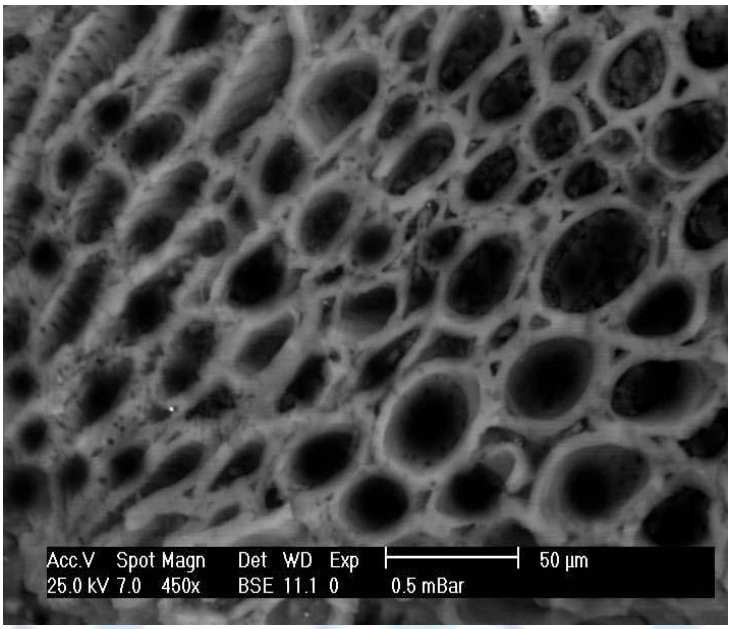

Fig.(2): SEM of date pits activated carbon

Treatment of surface and ground water samples.

The collected water samples were treated using prepared activated carbon to investigate its efficiency. Weight of 0.2 gm of activated carbon was shacked with 20 ml of water sample for 2 hr, and then the samples were centrifuged for 5 minutes at 5000 rpm and the supernatant of each sample was analyzed using AAS, as indicated in Table (2). It can be concluded that the residual concentration of treated elements from water by DP activated carbon was in agreement with WHO permissible limits.

Regeneration of used activated carbon

The reversibility of adsorption was investigated by carrying out desorption 190 experiments. Once equilibrium was reached, activated carbon saturated was removed from solution and transferred into stoppered 192 reagent bottles (250 mL capacity), containing 100 mL of (0.05 to 0.25 M) HCl solution 193 and the bottles were shaken at 150 rpm for 4 h at room temperature using a 194 mechanical shaker. The sorbent was then removed by centrifugation at 20000 g [12]. The concentrations of metal ions in the aqueous solutions were determined by AAS.

Comparative study:

Comparison of date pits activated carbon with commercial activated carbon was done, and the results indicated that using of prepared activated carbon for removal of Co, Sr, Cu, Cs, Pb, Cd, Ni, Fe, Zn was more effective than commercial activated carbon [13]

Table (4): Analysis of water samples after shaking with prepared activated carbon.

Metals	S No. 1	S No.2	S No. 3	S No.4	Permissible limit WHO 2008
Co	0.001	0.008	0.002	0.006	-
Sr	0.008	0.004	0.002	0.002	-
Cu	0.003	0.001	0.002	0.003	2.0
Cs	0.001	0.002	0.001	0.000	-
Pb	0.003	0.002	0.002	0.001	0.01
Cd	0.001	0.002	0.001	0.001	0.003
Ni	0.012	0.010	0.006	0.002	0.07
Fe	0.020	0.015	0.014	0.015	0.3
Zn	0.006	0.002	0.010	0.006	3.0
Cr	0.010	0.010	0.006	0.020	0.05

Conclusion

Date pits activated carbon is an effective adsorbant for removal of Co,Sr.Cu.Cs.Pb.Cd.Ni,Fe Cr at optimum conditions Weight of 0.2 gm of activated carbon was shacked with 20 ml of water sample for 2 hr, and then the samples were centrifuged for 5 minutes at 5000 rpm and it can be regenerated again.

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