

Adsorption of heavy metals by activated carbon synthesized from solid wastes.

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Abstract—Dates pits as a huge solid waste were used to prepare physically and chemically activated carbon. The raw materials were physically activated with steam (CS), while the chemically activated samples were prepared in the presence of zinc chloride (CZ) and phosphoric acid (CA), individually. The textural properties, including surface area, mean pore radius and total pore volume, were determined from the low temperature adsorption of nitrogen at 78 K. FT – IR spectroscopy and base neutralization capacity were used for the description of surface groups. The adsorption of heavy metals as pollutants, including Cu^{2+} , Mn^{2+} , Pb^{2+} , Fe^{3+} and Cd^{2+} was studied in a batch experiments.

The type and amount of used activator had considerable effects on the textural characteristics of investigated samples, i.e. it develops the porosity and therefore changes the textural properties. These changes of textural properties were associated with an excellent removal efficiency, exceeds 92 % and depending on the type of activator.

Index Terms—Adsorption, Activated carbon, Heavy metal, Solid waste.

I. INTRODUCTION

Industrial waste water represents the main source of environmental pollution with heavy metals, e.g. Cu, Pb, Fe, Cd, Mn, etc. Such metal may be discharged into the wastes from various industries, including metal plating, storage batteries, alloy industries, dyeing, textile, fertilizers and other chemical industries. The progressive increase of industrial technology results in continuous increase of pollution, so that a great effort has been devoted for minimizing these hazardous pollutants and therefore avoiding their dangerous effects of animals, plants and humans [1-7]. In brief, the enrichment of waste water with these metals beyond the healthy levels may causes a poisoning, leading to dysfunction of the kidney, reproductive system, liver, brain and also central nervous system [8]. The removals of these hazardous materials may be performed using various techniques, including precipitation [9], membrane filtration [10], ion exchange [11-12], sorptive flotation [13], and adsorption [1-7]. The removal of heavy metals via adsorption over solid adsorbents, e.g. activated carbons and others, is one of the most convenient methods used [14-21]. Activated carbon prepared from solid wastes still excellent adsorbents for many toxic materials present in the various types of waste water. This ability to arrest the

different pollutant molecules is mainly attributed to its higher specific surface area [21]. The recent trend is the preparation of activated carbons from various kinds of wastes [22-26], e.g. wood, coconut shell, nutshells, cotton stalks and wastes rubber. The selection of solid wastes as precursor for activated carbon depend on the potential for obtaining high quality activated carbon, presence of minimum inorganic, volume and cost of raw materials and storage life of raw materials. Dates pits is the major agricultural byproducts, produced in huge quantity from the main cultivated crop in Saudi Arabia, i.e. palm crop. All of these criteria stand behind on choosing the Dates pits as precursor for manufacture of activated carbon.

The present investigation aimed to:

1. Preparation of activated carbon from cheapest source.
2. Determination of the textural parameters, e.g. surface area, mean pore radius and total pore volume.
3. Using different techniques to specify the surface groups, namely Fourier Transform – Infrared spectroscopy (FT-IR) and the base neutralization capacity techniques.
4. Measurements of adsorption capacity of prepared active carbons.
5. Calculation of some adsorption parameters

II. MATERIALS & METHODS

Prior to the carbonization of raw materials, namely Dates pits, it was left in air for partial dryness, crushed to semi crystal fragments and then dried at 373K till constant weight. The dried crushed material was subjected to destructive distillation at 898K in tubular muffle furnace under flow of nitrogen for 5 hrs to obtain non – activated carbon (C).

A. Preparation of steam activated carbon (CS)

Three steam activated samples (CS27, CS38 and CS58) were prepared by gasification of non-activated carbon at 1173 K with steam in proper ratio of steam-nitrogen gas. The arabic numbers follow the letter S (steam) represent the percentage burn-off.

B. Preparation of Zinc chloride activated carbon (CZ)

In order to prepare Zinc chloride activated carbon (CZ2:1, CZ1:1 and CZ1:2), the dried samples was soaked in aqueous solution containing the appropriate amount of ZnCl_2 for 96 hrs. at 298K. The mixture was dried at 393K and then carbonized at 898K in stream of N_2 for 5 hrs. To remove the chloride ions, the carbonized samples were washed several times with double distilled water and then dried at 393K. The designation of the carbonization products depends on the weight ratio of raw material: ZnCl_2 , i.e. the sample CZ2:1 indicates a ratio of 2:1, while CZ1:1

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designates a ratio of 1:1.

C. Preparation of phosphoric acid activated carbon (CP)

The dried samples were soaked in aqueous solution containing the calculated amount of H₃PO₄ for 96 hrs. at 298K, followed by the same treatments received for CZ preparations where CP2:1, CP1:1 and CP1:2 activated samples were obtained.

D. Characterization of activated carbons

pH measurements

The pH value was determined using an Orion pH meter, after overnight shaking of 0.2 gm activated carbon in 25 ml by distilled water.

E. Base neutralization capacity (BNC)

BNC was determined via the adsorption from aqueous solutions of different bases, namely NaOH, Na₂CO₃ and NaHCO₃, onto prepared activated carbon. In Pyrex bottles, 0.2 gm sample in 50 ml (0.2 N) base was shaken for 24 hrs, filtered and then titrating the filtrate Vs. 0.1 N HCl.

F. Fourier Transform-Infrared spectroscopy (FT-IR)

FT-IR investigates the surface carbon-oxygen groups. The activated or unactivated carbon was diluted with KBr, compressed into wafer and FT-IR spectra were recorded by Mattson 5000 FT-IR spectrophotometer.

G. Surface area and pore texture

Surface area (SBET), mean pore diameter (d) and total pore volume (VP) were determined from low temperature adsorption of N₂ at 77K. Prior to adsorption measurements, the sample was activated at 473K for 2 hrs, under a reduced pressure of 10-6 torr.

H. Adsorption of pollutants & Adsorption of heavy metals:

The adsorption of Fe, Pb, Cu and Cd was followed in a static batch experiment, considering the same procedure described for phenol adsorption, where the concentration of un-adsorbed Cu²⁺ and Cd²⁺ was determined using atomic absorption.

III. RESULTS AND DISCUSSIONS

The measurement of pH values for the supernatants of all investigated carbons reveals that steam activated carbon prepared at 1173 are basic (~9.4), while zinc chloride activated carbons are acidic carbon (~ 4.3). FT-IR spectrum of un-activated(C), H₃PO₄-activated (CP) and ZnCl₂-activated carbons (CZ) is depicted in Fig. (1). FT-IR of the un-activated carbon show band at 1246 cm⁻¹, predicting the presence of phenolic and lactonic groups, while - O - H group may be indicated from the bands in the region 1377 - 1447. The absorption bands assigned in the region 1520 - 1622 may be attributed to quinonic and carboxylate groups [1,14,27-29]. For steam activated, slight shifts of weak absorption bands characterizing the previous reported groups were found. Moreover, some of the detected absorption bands either disappeared or became less predominant. This can be taken as evidence for the decrease of surface acidity upon activating with steam, whereas the basic group became more predominant. Zinc chloride

activated carbons depicts different FT-IR spectra, corresponding different groups, as predicted from the bands 650 (aromatic C - H region), 1050 (= C = O stretching vibration), 1125 (phenolic and lactonic group), 1550 and 1650 cm⁻¹ (quinonic and carboxylate groups). H₃PO₄ activated carbons exhibits FT-IR spectra including 4 absorption bands centered at 750, 1660, 2600 and 3567 cm⁻¹. These bands correspond to aromatic C-H region, free carboxylic group, and -OH group overlapped with physisorbed water (H₂O). It should be mentioned that, the slight shift in wave number associated with a particular group may be attributed to the different activation mechanisms results from physical and chemical activation. Base neutralization capacities is the most simplest and convenient technique for the qualitative and quantitative identification of surface acidic groups on the surface of active carbons [30]. It was found that the titration with Na₂CO₃ can neutralize carboxylic and lactonic groups, NaHCO₃, neutralize the carboxylic groups while NaOH neutralizes all acidic groups on the surface. The base neutralization capacities of the investigated samples expressed as equiv./gm are listed in table (1).

TABLE 1: BASE NEUTRALIZATION CAPACITIES OF VARIOUS CARBON STUDIED-

Samples	Na ₂ CO ₃ meqv/g	NaHCO ₃ meqv/g	NaOH meqv/g
CSII	0.51	0.07	0.7
CZ 1:1	5.5	5.3	13
CA 1:1	6.58	5.4	12.6

Table 1 predicts that: (i) CS samples are less acidic, confirming thus the data obtained from FT-IR in creating some basic group for steam activated activated carbons, where the total meqv./ gm for surface acidic groups ~ 0.6. The type of the acidic groups follows the order lactonic > phenolic > carboxylic, (ii) zinc chloride- and H₃PO₄ - activated carbons are rich with lactones, while phenols and carboxylic groups are less predominant and having relatively the same magnitude. The adsorption / desorption isotherms of nitrogen on all investigated carbons at 77K are depicted in Fig. (2). Comparing the time required to establish equilibrium during adsorption of nitrogen on both unactivated and activated carbons, a long time elapsed to inactivated carbon to indicate the presence of ultrafine pores in which nitrogen diffused with higher diffusion energy [31,32]. In contrary, the activation of carbons with different activators, i.e. steam, ZnCl₂ and H₃PO₄, led to rapid adsorption with equilibrium time 15 - 20 min.

The specific surface area (m²/g), column 2 of table 2, as calculated from N₂ adsorption isotherms, adopting 0.162 nm² as cross sectional area of nitrogen molecule [33] and using the BET equation [34],

$$\frac{P}{V(P_0 - P)} = \left\{ \frac{1}{V_m C} + \left[\frac{C - 1}{V_m C} \right] \frac{P}{P_0} \right\}$$
 where P is the equilibrium pressure, P₀ the saturated vapor pressure and V the adsorbed volume at pressure P.

The total pore volume (VT) and the mean pore diameter (d) are another two textural parameters given by the relationships:

$$VT \text{ (ml/g)} = V_{\text{sat.}} \times 15.47 \times 10^{-4}$$

$$d \text{ (nm)} = (4 VT / SBET) \times 10^{-3}$$

where V_{sat.} represent the amount of nitrogen adsorbed near saturation, i.e. at P/P₀ 1.0

An alternative two methods for estimating specific surface area are:

• VI-t method called t-curves which represent the plot of Vads. in ml Vs. the statistical thickness of adsorbed film at relative pressure P/P_0 , where St = slope of the straight line passing through the origin $\times 104$

• α - method depends on the plot of Vads. (CC/g) Vs. the standard values of α for non-porous solid, where $S\alpha$ = slope of the straight line passing through the origin $\times 2.84$

Inspection of table 2 predicts that:

(i) The SBET of nonactivated carbon (C) amounts to 9.9 m²/g, indicating the presence of narrow pores which accessible to nitrogen molecules at 77K.

(ii) A good agreement between SBET, $S\alpha$ and St indicates the successful choice of the standard isotherm and thet-values.

TABLE (2): SOME ADSORPTION PARAMETERS OBTAINED FROM THE APPLICATION OF BET EQUATION:

Samples	$S_{BET}(m^2/g)$	$V_T(ml/g)$	$d(nm)$	$S_t(m^2/g)$	$S_\alpha(m^2/g)$	$S_{micro}(m^2/g)$
C	9.8	0.006	1.02	9.6	9.3	6.73
CSI	595	0.298	1.02	596	590	532
CSII	1105	0.5644	1.03	1105	1111	950
CSIII	978	0.4828	1	980	984	841
CZ2:1	715	0.3608	1.02	714	722	643
CZ1:1	754	0.3762	1.1	755	749	627
CZ1:2	1175	0.5952	1.02	1177	1175	757
CP2:1	205	0.1039	1.02	206	214	166
CP1:1	241	0.1221	1.03	242	241	136
CP1:2	578	0.2924	1.02	580	575	260

(iii) The increase of burn-off up to 56% for steam activated carbon led to a decrease of specific surface area. This may be explained from the creation mainly microspores structures, while the increase of burn-off beyond certain level results in a contribution of some mesopores to SBET.

(iv) Generally, the physical and chemical activation, i.e. steam, $ZnCl_2$ or H_3PO_4 , enhanced the porosity and therefore results in a pronounced increase of total pore volume and specific surface area. This may be explained on the basis of different activation mechanism. Firstly, the pyrolysis of the raw materials enhanced the cross-linking and hence creates a highly porous materials. Dubinin and others approved that the activation with metal halide produced a tar-free texture by forming HX [35,36]. On the other side the activation with phosphoric acid led to elimination of water and therefore destruction of cellulosic structure [37].

(v) The increase of amount of activators was associated with increase of total pore volume and specific surface area, whereas the mean pore radius predominantly decreased, assuming a great contribution of microspores to the total pore volume. This may be evident from the diameter of majority of pores of < 2 nm.

A. Adsorption of heavy metals

Some effort in Saudi Arabia has been devoted to evaluate the contamination of ground and/or surface water with heavy metals, approving very low concentrations of the heavy metals not exceeds 20 ppm [38,39] at Unaizah, Al-Hasa and Al-Kharj cities. Fe and Mn is the most predominant in all mentioned cities and measured approximately 68 (Mn) and 112 ppm (Fe). The removal of

such or even higher concentrations can be carried out successfully by our home made activated carbons. The adsorption isotherms of some selected heavy metals on the investigated carbon at 298 K are representatively depicted in Fig. All isotherms are of type L according to Giles classification [40], Figs. (3-5) and exhibit a slight increase of adsorption beyond the plateau region. The variation of adsorption capacity with concentration of adsorbates can be discussed with the aid of Freundlich and Langmuir relationships.

The adsorption data were applied satisfactorily to Freundlich equation:

$$\log Y = \log KF + 1/n \log C_{eqm}.$$

where $Y = X/m$ is the amount of adsorbate [ppm.gm-1.l-1], C_{eqm} is the equilibrium concentration, while n and KF are empirical Freundlich constants as determined from the slope and intercept for the good linear plot of $\log Y$ Vs. $\log C_{eqm}$, Fig. (6-7). The values of these constants, listed in table 3, account for the affinity of adsorption of various adsorbates on to the present activated carbons. In other words, the increase of KF and n may indicate a higher adsorption capacity. Another equation for determining the adsorption capacity for the home made activated carbon is the following Langmuir equation:

$$C/Y = (a/Y_m) + (C/Y_m)$$

where a is the langmuir adsorption parameter and Y_m is the monolayer capacity, table 3.

Inspection of the data listed in table2 dealing with the Freundlich parameters, reveals that:

TABLE (3): FREUNDLICH PARAMETERS FOR THE ADSORPTION OF HEAVY METALS ON VARIOUS ACTIVATED CARBON SAMPLES (AT 299 K)

Adsorbate	Parameters	CS27	CS38	CS56	CZ2:1	CZ1:1	CZ1:2
Fe	n	3.86	5.63	6.05	3.04	2.66	3.83
	Kf	25587	27321	28547	28908	30904	34199
Cu	n	0.2	0.89	0.89	0.0615	0.0693	0.0338
	Kf	3.7	1001	5623	50118	31623	28185
Pb	n	10.54	7.36	6.63	12.82	16.48	22.14
	Kf	26916	38020	31334	29988	36788	45383
Cd	n	2.38	7.48	10.3	15.49	20.54	26.90
	Kf	2885	13439	15327	30875	39420	49682

1.The values of KF and n increase generally for the adsorption of heavy metals to either CS or CZ samples. This may be discussed in terms of increasing of SBET with increasing the amount of activators led to increasing of the amount adsorbed. Thus, the specific surface area is an important factor in determining the amount of adsorbate at adsorbate / adsorbent interface and thereby affects to great extent the adsorption capacities.

2.The slight fluctuation in the value of freundlich constant may be related to the presence of various functional groups, i.e. the surface of active carbon is

naturally heterogeneous [41].

3.The higher values of n than unity may be referred to the significant adsorption occurred at lower concentrations.

4.Zinc chloride-activated carbon owned higher adsorption capacities for heavy metals compared with steam-activated carbons ones. This behavior may be interpreted in term of higher porosity and therefore facilitate the diffusion of metal ions. The values of monolayer capacity for the adsorption of heavy metals, expressed in m.moles/gm could be evaluated using Langmiur relationship,table4.

TABLE (4): LANGMUIR PARAMETERS FOR THE ADSORPTION OF HEAVY METALS ON VARIOUS ACTIVATED CARBONS (AT 299 K)

Adsorbate	Parameters	CS27	CS38	CS56	CZ2:1	CZ1:1	CZ1:2
Fe	Ym	2.90	4.19	3.73	42.74	43	41
Cu	Ym	3.5	6.13	3.97	39	36	38.09
Pb	Ym	3.9	5.91	5.4	44	46.02	48
Cd	Ym	4.5	14.36	12.55	45	47.08	57

An insight on the values of monolayer capacity (Ym) summarizes that

1.A general trend for increasing these values upon increasing the amount of activators is observed.

2.Zinc chloride-activated carbon owned higher Ym values compared with steam-activated carbons ones. This behavior may be interpreted in term of higher porosity and therefore facilitate the diffusion of metalions.

3.The decrease of Ym for CS56 samples may be correlated with the slight decrease of surface area.

4.The order of removal efficiency of investigated heavy metals via theadsorption onto CS carbons was found to be: Cd > Pb > Cu > Fe,whereas CZ samples exhibits the order of Cd > Pb > Fe > Cu.

IV. CONCLUSIONS

An insight on our finding, the results can be summarized in:

1.The non-activated carbon (C) having the lower surface area accessible for different adsorbates, whereas the physical and chemical activation was associated with an increase of total pore volume and specific surface area. The development of porous.Structure may be reviewed to the destruction of cellulosic materials to create a microspore structure.

2. FT-IR for un-activated carbon indicates the presence of phenolic,lactonic, quinonic and carboxyl ate groups. Steam activation led to a decrease of surface acidity whereas the basic group became more predominant. Zinc chloride activated carbons depict different FT-IR spectra, corresponding different predominating acidic groups.

3.The specific surface area was found as a predominant factor in determining the adsorption capacity of investigated carbons. Generally, CZ samples having a higher adsorption power than CS carbons for the removal of heavy metals.

4.The home made carbons exhibits high removal efficiency reaching 99% activity for some samples, particularly for lower concentrations.

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REFERENCES

- [1] E. A. El-Sharkawy, Ads. Sci. & Technol. 19 (2001) 795.
- [2] A. M. Youssef, A. M. El-Wakil, E. A. El-Sharkawy, A.B. Farag, Ads.Sci. & Technol. 13 (1996) 115.
- [3] A. Aklil, M. Mouflih, S. Sebt, J. Hazardous Materials A112 (2004) 183.
- [4] A.M. Youssef, Th-El-Nabarawy, S.E. Samra, Colloids and Surfaces A:235 (2004) 153.
- [5] A. Jang, Y. Seo, P. L. Bishop, Environmental pollution 133 (2005) 117.
- [6] D. Zhou, L. Zhang, J. Zhou, S. Guo, Water Research 38 (2004) 2643.
- [7] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Bioresource Technol. 76 (2001) 63.
- [8] S.Senthilkumar,S.Bharathi,D.Nithyanandhi,V.Subburam,Bioresource Technol. 75 (2000) 163.
- [9] K. D. Linstedt, C. P. Houok, J. T. O'Connor, J. Water Pollut. Control Fed. 43 (1981) 1507.
- [10] P. S. Cartwright, Plating Surf. Fin. 68 (1981) 40.
- [11] EAA Economic of wastewater treatment alternative for the electroplating industry, EPA technology transfer, 1979.
- [12] T. L. Jester, T. H. Taylor, Proceedings of the 28th purdue industrial waste conference 28 (1973) 129.
- [13] S. E. Ghazy, S. E. Samra, S. M. El-Morsy, Adsorption Sci. & Technol.19 (2001) 721.
- [14] M.M. Abou-Mesalam, Colloids and Surfaces A: 225 (2003) 85.
- [15] VK. Gupta, I. Ali, Encyclopedia of surface and colloid science, NewYork: Marcel Dekker, 2002, P. 136-46.
- [16] SK. Srivastava, R. Tyagi, Water Res. 29 (1995) 483.
- [17] JT. Paprowicz, Environ. Technol. 11 (1990) 71.
- [18] VK. Gupta, D. Mohan, M. Sharma, S. Sharma, Sepn. Sci. Technol. 35(2000) 2097.
- [19] S.M. Koh, J.B. Dioxan, Appl. Clay Sci. 18 (2001) 111.
- [20] PZ Wu, ZW Liao, HF Zhang, JG Guo, Environ. Intern. 26 (2001) 401.
- [21] R.C. Banzal, J.B. Donnet, F. Stoeckli, Active Carbon, Marcel Dekker,New York/Basel (1988).
- [22] A. Netzer, P. Wilkinson, S. Beszedits, Water Res. 8 (1974) 813.
- [23] I.Vilbascusa, M. Martinez, N. Miralles, J. Chem. Technol. Biotechnol.75 (2000) 812.
- [24] M.N. Alaya, M.A. Hourieh, A.M. Youssef, F.A. Sejariah, Ads. Sci. &Technol. 18 (2000) 27.

- [25] M.N. Alaya, M.A. Hourieh, F.A. Sejariah, A.M. Youssef, Ads. Sci. & Technol. 19 (2001) 321.
 - [26] M.A. Hourieh, M.N. Alaya, A.M. Youssef, F.A. Sejariah, Ads. Sci. & Technol. 17 (1999) 675.
 - [27] J.V. Hallum, H.V. Drushel, J. Phys. Chem. 62 (1952) 110.
 - [28] V.A. Garten, D.E. Weiss, Rev. Pure Appli. Chem. 7 (1957) 69.
 - [29] C. Ishizaki, I. Marti, Carbon 19 (1981) 409.
 - [30] H.P. Boehm, Adv. Catal. 16 (1966) 176.
 - [31] R.B. Anderson, W.K. Hall, J. A. Lecky, K.C. Stein, J. Phys. Chem. 60(1965) 1548.
 - [32] P. Chiche, S. Durif, S. Pregermain 44 (1965) 5.
 - [33] D.M. Yong, P.A. Crowell, Physical adsorption of gases, Butterworths, London (1962) P. 226.
 - [34] S. Brunauer, P.H. Emmet, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.
 - [35] M.M. Dubinin, Conf. Ind. Carbon and Graphite, Soc. of Chem. Ind.(1958) 219.
 - [36] M.M. Dubinin, L.V. Radushkevich, Proc. Acad. Sci. USSR 53 (1947)33.
 - [37] H. Juentgen, Carbon 15 (1977) 273.
 - [38] J. Devi Prasad, I. I. Bashour, A. Al-Shanghitti, H. Austin, Regional Agriculture and Water Research Center, Ministry of Agriculture and Water, Riyadh, Saudi Arabia.
 - [39] J. Devi Prasad, I. I. Bashour, A. Al-Shanghitti, Regional Agriculture and Water Research Center at Ministry of Agriculture and Water, Riyadh, Saudi Arabia, Arab Gulf J. Scient. Res. 2 (1984) 259.
 - [40] C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, J. Chem. Soc.(1960) P. 3973.
 - [41] T. Hsisheng, H. Chien-To, J. Chem. Technol. Biotechnol. 74 (1999)123.
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