AGRICULTURAL WASTES AND ACTIVATED CARBON FROM THEM FOR FURFURAL REMOVAL FROM WATER SOLUTIONS

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Abstract. In this paper it has been introduced furfural reduction from water solutions as more important substances for chemical synthesis and as solvent extraction in petroleum refineries. This organic compound entering in soil and water system are considered such a serious problem is that all have some acut and long term toxic effects. The results of research in the field of using of activated carbon produced from agricultural wastes, as sorbents and as promising materials for wastewater treatment from furfural. The advantages of activated carbon produced from agricultural wastes in comparison with other sorbents are their low cost, availability of extraction and others. Apricot stones based acid-activated carbon has higher sorptive activity.The sorption activity of this sorbent as well as comparable with the commercial carbon.
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1. Introduction

To day water pollution is one of the most important environmental problems in the world. There are many sources of toxic chemicals in the environment, such as industrial pollution and pesticides runoff. However, industrial pollution wastewater is an important point source of water pollution. Most of industrial wastewater contains organics which are difficult or impossible to remove by conventional biological treatment processes, which are used in the most industries in the world [1]. Many technologies have been developed over the years to treat industrial wastewater contain material which are refractive or potentially toxic to biological growth [2].

One of the best methods for wastewater treatment and water purification from organic and inorganic polutant is an application of suitable absorbent. Activated carbon (AC) because of its high adsorptive capacity has become one of the most technically important and most widely used adsorbents[3,4].The increasing demand for sorptive materials as ecological problems simulated the intensive study of agricultural by-products waste precursor, because they are considered to be cheap sorbent and also good source for AC production[5]. AC is obtained from carefully contolled process of dehydration, carbonization and oxidation of organic substances. It can be prepared for research in laboratory from a large number of materials. However, the most commonly used ones in commercial practice are peat, coal, lignite, wood and agricultural by-products such as rice husks, bagass, fruit stones and shell of coconut, almond, etc.[6].

The usage of carbon adsorbents depend on their surface area, pore size distribution and chemical characteristics.The mentioned quality of AC are directly related to the nature of starting material, the type of the production method and the temperature of production[6]. In general, an AC which is used in any of the most common aplication must have adequate adsorptive capacity, chemical purity, mechanical strength and etc.[7,8].

Depending on the starting material AC may contain some impurities. Therefore, the adsorption characteristics of AC for certain uses are influenced by the ash content.So the raw material should contain as small ash as possible and also the raw material must have relatively low cost. Although agricultural wastes are the major raw materials used, they have very high volatile content and hence give low yields of AC, but they are relatively inexpensive and economical starting materials [8].

Furfural (FF) is an aromatic aldehyde with the chemical formula C_4H_3OCHO. The main use of furfural is in the form of feed stock for furfural alcohol (FFA) (accounting for 75 % of FFsales), which in turn, is used as input for furan resin, which are used for foundry binders [9]. Guillermo Rodriguez et al., 2008 reported that world market for FF and FFA is around 300,000 tones / year with annual growth of about 2 % per year. It is consumed by the chemical industries as intermediate products such as nylons, lubricants and solvents, adhesive, medicines, and plastics. Major use (perhaps 65 % or more of world consumption) is for urea furan resine synthesis; a binding material in metallurgy, precision casts and dies [10].

Furfural is also used as solvent in petrochemical refining to extract dines and aromatics from other hydrocarbons. 13% of furfural is used as additional processing solvent, generally in petrol chemistry – for butadiene separation from oil cracking gases, for refining of plant oils and lubricating oils. Furfural is also an intermediate in the production of the solvents [10].

In short – term exposure, furfural may cause irritation of the skin, eyes and respiratory tract. It may also cause a person to become unconscious. In long-term exposure, it may cause sensitization of skin, loss of taste, and numbness of tongue, furfural vapor is irritating to the eyes. Its odor threshold is 0.25-0.38 ppm[11] . Furfural actuate exposure can also damage the liver and kidneys and to tumors and mutations. The Permissible Exposure Limit (PEL) and the threshold limit value (TLV) for furfural was reported 5.0µg/ml and 2.0µg/ml, respectively ([12 and 13].

Actuate toxicity: The oral LD_{50} for furfural was reported 127mg/kgbw in rates ([14]and 333 mg/kgbw in mice [15].

Presence of furfural, increase the toxicity of wastewater and makes biological treatment very difficult. Removal of this substance will require modifications or alternatives of the existing systems [16].This compound if discharge in open revers, it can destroy the micro flora and has negative effect on human health. In order to eliminate or lowering the concentration of wide range of dissolved pollutants (organic and inorganic) in an effluent, adsorption is widely used as an effective physical method of separation. Activated carbon (AC) is a well known adsorbent that can be used efficiently for removal of broad spectrum of pollutants from air, soil, and liquids. Adsorbents are usually porous solids, and adsorption occurs mainly on the pore walls inside particles. AC is effectively eliminated many pollutants (organic, inorganic and biological) in water and wastewater treatment. [17]. In presnt paper it has been investigated an adsorptive abilities of activated carbon produced from agricultural wastes in relation to furfural pollutants. The major way to diminish the discharge of furfural dissolved in water is stronger purification.

The objective of the present study is to describe, experimentally, the potential of activated carbon produced from agricultural waste to adsorb organic pollutants using furfural as model component.

MATERIALS AND METHODS

The abundance and availability of agricultural waste as apricot, peach stones and based on them activated carbon; make them good candidates as precursors for activated carbons. It has been exist rare literature on the use of agricultural waste and base on them activated carbon for furfural adsorption from water and wastewater treatment processes.

The sample used in this study consisted of:

(A) Tow experimental carbons, namely

1. Peach stones based activated carbon
2. Apricot stones based activated carbon

(B) One commercial activated carbon, namely Carbonsorb-AB

This carbon was selected as control for this experiment as they have found to poss the desirable physical and chemical characteristics and was extensively used in municipal wastewater treatment facilities.

A process for treating wastewater realized through the use of powdered activated carbon, which is can be responsible;

1. for physically removing of colloidal and suspended volatile solids through adsorption;
2. for adsorbing of organic substances and elements that interfere with biological processes, thus serving to reduce their contact with and exposure to activated sludge organisms effecting wastewater treatment functions;
3. for providing fixed surface in activated sludge wastewater treatment bioreactors for bacteria and other organisms.

Bulk density

Bulk density is an important criterion for consideration in the designing of adsorption towers for use in pilot plant studies as well as large commercial applications. For activated carbon, for instance, the adsorption rate is influenced by carbon particle size, which again drpends on the bulk density of the granular activated carbon. During municipal wastewater treatment the residence time of the wastewater in the coloumn containing granular activated carbon is affected by the bulk density(ρ) as shown by the equation:

$$R_s = \frac{pAvr}{7.48T}$$

Where, R_s –carbon usage rate ($lb/ft^2 min$)

ρ - Bulk density of the GAC (lb/ft^3)

A – Adsorber cross-section area (lb/ft^2)

V – Linear flow rate (gallons/min/ft)

r – Residence time (min), and

T- Processing time (perrich, 1981)

Attrition or hardness measures the mechanical strength and determins activated carbon and agricultural by-products ability to withstand normal handling operatins.

Measurement of physical properties of sorbents total surface area (m^2/g)

The total surface area of the activated carbons was determined by the method pendyal [3], using Micromeritics Gemini 2375 surface area analyzer. The total surface area was measured by nitrogen adsorption at 77^0K using 15 point BET.

Determination of Bulk Density (g/m^3)

For agricultural by-products and activated carbon from them bulk density was measured using the method[3], which consisted of placing a known weight of granular activated carbon of 10-30 mesh size carbon in a 25 ml cylinder to a specified volume and tapping the cylinder fo at least 1-2 min and measuring the volume of carbon. The bulk density was measured as:

$$Bulk\ density(g/cm^3) = \frac{weight\ of\ dry\ sample\ (g)}{Volume\ of\ packed\ dry\ sample\ (cm^3)}$$

Determination of Attrition/ Hardness (%)

The attrition of the samples was measured using wet attrition method described [3]. One gram of granular activated carbon of 10-30 mesh was added to 100 ml of acetate buffer (0.07 M sodium acetate and 0.03 M acetic acid, pH 4.8) in a 150 ml beaker. The solution was stirred at 500 rpm for 24 h, with a ½ inch stir bar for agitation. The solution was then filtered through 50-mesh screen and the retained carbon was throughly washed and dried at 90^0c under vacuum for 4 h and weighed. The % attrition was measured as:

$$\text{Attrition (\%)} = \frac{\text{Initial weight(g)} - \text{Final weight(g)}}{\text{Initial weight(g)}} * 100.$$

3.11. Determination of ash content

Ash content (% ash) was determined by the method of Ahmedna et al. (1997). Approximately 2 g of powdered activated carbon was placed into weighed ceramic crucibles.
Carbon and crucibles were dried overnight at 80^0C and reweighed to obtain the dry carbon weight.

The samples were heated in a muffle furnace at 575^0 C for 12 hours or overnight. The crucibles were cooled in a desiccator, and remaining solids (ash) were weighed. Percent ash was calculated by:

% ash = [remaining solids wt (g) / original carbon wt (g)] X 100

Result and Discussion

Adsorption of furfural from water solutions: The furfural measurements were carried out in concentration 0.01 M. One gram of sorbent added on 100 ml solutions of furfural in water. The mix was carefully shaken up within 4 hours. The measurements of molar refraction of a solution were carried out before and after sorption, on a difference of concentration of adsorbed furfural. Furfural concentration was measured using UV adsorption-spectrum at 270 nm (Shimdzu). Residual quantities of furfural were determined by liquid chromatography and UV spectrum also. It is necessary to note that partial sorption of water /1-2 ml from 10 ml of solution takes place for 4 hours sorption of a solution on sorbents. The results are similarly, apricot stones based acid-activated carbon has higher sportive activity. It also followed expect, as this sorbent has higher physical indicators. The sorption activity of mentioned sorbent as well as comparable with the commercial carbon – Carbonsrb-AB. The results are given in the Table 1.

Properties of peach and apricot stones

The both of them were obtained from the garden in Ararat valley. Elemental analysis of stones and activated carbon from them were determined using an "Elemental analyzer", physical properties and chemical composition of the using materials is given in Table 2. Activated carbon can contain some impurities depending on the type of using stones. In this case it should be clean before the using, it make here. Also, the row materials and the activated carbon should contain as small ash as possible.Adsorption by activated carbon produced from agricultural wastes is preferred, because of its have low sensitivity to flow fluctuations and exhibits greater flexibility. The advantages of powdered activated carbon produced from agricultural waste in comparison with other sorbents are their low cost, availability of extraction, operational flexibility, control, etc.The effectiveness of agricultural by-products adsorption also is enhanced made activated carbon for the removal of

organics by its large surface area resulting in higher separation efficiency by activated carbon.

Activated carbon surface area has nonpolar nature, but during the treatment process with some chemicals, as acids for instance, this sorbents surface took slightly polor character, which is in future can be responsible for hydrophobic influence of this surface. In this case, as raw stone materials and more activated carbon can be used for organic molecule sorbents [4].It should be noted also it' s known, that activated carbon obtained from fruit stones can favorably compared with other activated carbons used in industry with respect of their properties. Here, as it is possible is take place the physical adsorption which is held on the surface of stones or activated carbon, which have not active sites on the surface, by weak van der waals forces.

Table 1. Reduction of furfural 100 ml 0.01 M furfural on activated carbon /1g, temperature 20^0C, duration 4 hours

N	Sorbent	The adsorption mg/g
1	Peach seeds based activated carbon	0.29
2	Apricot seeds based acid-activated	0.32
3	Carbonsorb - AB	0.36

Table2. Physical and chemichal properties of experimental sorbents

Physical properties	Row peach stones breaking	Row apricot stones breaking	Peach stones activated carbon	Apricot stones activated carbon
Surface area (m^2/g)	220	250	620	710
Bulk density (g/m^3)	-	-	0.41	0.46
Attrition (%)	-	-	11.3	8.60
Elemental analysis Result (%)				
C	48.0	50.0	74.0	85.0
H	6.0	5.0	2.5	2.0
O	46.0	45.0	18.0	8.0
Ash	-	-	5.5	5.0

Conclusion

It has been found advantageous to go on with the researches in organic pollutants sorption by agricultural wastes and based them activated carbons. It has been offered the convenient method for successfully sorption furfural and probably other organic substances as BTEX/ benzene, ethyl benzene, toluene and xylems' /, pesticides from petroleum and petroleum industry having countries for wastewater treatment from furfural.

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