LINGOCELLULOSICS: CONVENIENT SORBENTS FOR WASTE WATER TREATMENT FROM PHENOL AND FUFURAL

G.H.Torosyan[1], Ghazi Aidan[2], D.N.Hovhannisyan[3]

[1] *State Engineering University of Armenia, department of chemical technology & environmental engineering, Yerevan, Armenia, email: gagiktorosyan@seua.am*
[2] *Institute of Geological Sciences of Academy of Sciences of Armenia, Yerevan*
[3] *Yerevan State University of Architecture & Construction, Yerevan, Armenia & European Regional Educational Academy, Yerevan, Armenia*

Abstract.*In this paper it has been introduced phenol and furfural sorption from water solutions as more important substances for chemical synthesis and as solvent in specially for oil refining solvent and the results of research in the field of the using of natural materials – as agricultural by-products, activated carbon from them as sorbents and as promising materials for waste water treatment from phenol and furfural. The advantages of agricultural by-products in comparison with other sorbents are their low cost, availability of extraction and others.*

Phenol and furfural exist in significant percentage of petroleum products as solvent and refining agent. This organic compound entering in soil and groundwater system are considered such a serious problem is that all have some acute and long term toxic effects.

Apricot stones based acid-activated carbon has higher sorptive activity. The sorption activity of this sorbent as well as comparable with the commercial carbon - Carbonsorb-AB.

Keywords: *natural materials, water solution, phenol, furfural, oil products, agricultural by-product, fruit stones and based on them activated carbon, adsorption, adsorbent, wastewater treatment,.*

Introduction

Organic compounds can be major pollution problem in soil and groundwater. Their presence in water can create a hazard to public health and the environment. Soil and groundwater pollution from enterprises which have a relation with petroleum and this type of other products is becoming an important topic of interest as a result of the increasing public and regulatory concerns worldwide with problems of groundwater contamination and resultant impact on human health and ecological systems.

Phenols, furfural make up a significant percentage of petroleum products. This organic compounds entering in soil and groundwater system are considered such a serious problem is that all have some acute and long term toxic effects.

Taking into account that fact, that some of enterprises have no while the appropriate means, here is offer the elementary technological circuit of clearing of drains, for instance special holes with the boxes, filled in them by activated carbon. Waste water here flows down which further are removed and are burnt in furnaces. The offered circuit already has worked at several stations on sale of combustible materials.

One of the best method for wastewater treatment from organic pollutants is an application of inorganic and organic adsorbents. Absorption of organic compounds from water solutions with application of sorbents on the basis of a waste of agricultural products – soft lingocellulosic precursors as shells of nuts and fruit stones had been investigated. The increasing demand for sorptive materials as ecological problems simulated the intensive study of lingocellulosic precursors because they are considered to be cheep sorbents and also source for activated carbon obtaining [1-5]. Activated carbon has been utilized as chemical sieves, gas absorbers, odor control and filters in water and wastewater treatment processes.

The technological stability of lingocellulosic precursors is determined first of all by such characteristics as mineral and chemical composition, sorption ability and then mechanical, physical and following from them filtering properties [5]. High performance lingocellulosic materials with uniform densities, durability in adverse environment and high strength can be produced by using as bonding agents the important issues for adsorption processes. The other sites the wide distribution, renewability and recyclability of lingocellulosics can be expend the market for low-cost materials.

The advantages of lingocellulosic precursors in comparison with other sorbents are their reserves in agricultural developing countries as Armenia, a unique complex of technological properties as well as their natural origin, possibilities of they modification in activated, and utilization [5]. The application of lingocellulosic precursors in the processes of water preparation has been scientifically approved according to the all-round evaluation of physical-chemical, technological properties of agricultural by products developed. It has been established that the lingocellulosic precursors and activated carbon are necessary to remove metal ions from water. It have been established the regularities of extraction processes of ions of iron, magnesium, calcium, zinc, copper, nickel, cobalt, lead and ammonium from water. The dependence of efficiency and mechanism of sorption of components from water, filtering parameters, length of contact liquid and solid phases ratio and other factors are obtained.

In present paper it has been investigated the phenols and furfural sorption from water solution. That compounds are discharged in open reservoirs, they destroy the microflora and have negative effect on human health. The major way to diminish the discharge of phenols, also furfural dissolved in water is strong purification and reuse.

Experimental part

The using agricultural by-product in present research

The abundance and availability of agricultural by-products / the using by-products in this investigation apricot, peach stones and based on them activated carbon / make them good candidates as precursors for activated carbons. It has been exists rare literature on the use of agricultural by-product and based on them activated carbon for wastewater treatment processes.

The samples used in this study consisted of:

(A) Four experimental carbons, namely

1. Row peach stones breaking,
2. Peach seeds based acid-activated carbon,
3. Row apricot stones breaking,
4. Apricot seeds based acid-activated carbon.

One commercial carbons, namely Carbonsorb-AB

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

A process for treating wastewater realized through the use of powdered natural ligno-cellulosic materials, 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 surfaces in activated sludge wastewater treatment bioreactors for bacteria and other organisms.

Adsorption of phenol from water solutions:

Polluted by phenol water had passed through column filled with adsorbents. Phenol had taken from water, remaining in limits of adsorption column. The treated water leaves a column for direct use or further treatment.

The higher adsorptivity shows apricot stones based acid-activated carbon The linear dependence between concentration of phenol in a water solution and appropriate molar refraction is preset at 20^{o}C. The measurements were carried out in concentration limits from 0,01 up to 0,05 mol/L. It was earlier established, that the sorption in these limits grows and has linear dependence on molar refraction. From graphic dependence is determined amount of adsorpted phenol. The results are given in the Table 2. It is necessary to note, that partial sorption of water /1-2ml from 10ml of a solution for 4 hours sorption of a solution on sorbents / takes place. It's visible from the given tables with increase of concentration of solutions the amount of absorbed phenol is increased.

Adsorption of furfural from water solutions: On 1 gr of sorbent added on 100ml 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 an organic solution expected amount of adsorpted furfural.Here it has been check the results by liquid chromatography and UV spectrum dates also. The results are given in the Table 3.

Properties 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 a " Elemental analyzer". Chemical composition of the using materials is given in table 1.

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 Equilibria.

Adsorption from wastewater with organic pollutants involves concentration of the solute on the surface. Here, it has been had adsorption and desorption process together which will attain an equilibrium state. We used Freundlich model for description of the adsorption data for zeolites and activated carbon.

It`s known, that the Freundlich adsorption equation is the most widely

used mathematical description for aqueous systems.

We use here the Freundlich equation is written in logarithmic form.

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C_e$$

Where,

x - amount of organic adsorbted

m - the weight of adsorbent

Ce - the solute equilibrium concentration

K, 1/n - constants characteristic of the system.

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 depends on the bulk density of the granular activated carbon. During municipal wastewater treatment the residence time of the wastewater in the column containing granular activated carbon is affected by the bulk density (ρ) as shown by the equation:

$$R_s = \frac{\rho A \nu r}{7.48T}$$

Where, Rs - carbon usage rate (lb/ft2 min)

ρ - bulk density of the GAC (lb/ft3)

A - adsorber cross-section area (lb/ft2)

ν - linear flow rate (gallons/min/ft)

r - residence time (min.), and

T - processing time (Perrich, 1981).

Attrition or hardness measures the mechanical strength and determines zeolites and activated carbon (agricultural by-products) ability to withstand normal handling operations.

Methods: The measurement of physical & mechanical properties for investigated sorbents

A. Measurement of physical properties of sorbents total surface area (m2/g/)

The total surface area of the activated carbons was determined by the method Pendyal et al. (1999) using Micromeritics Gemini 2375 surface area analyzer. The total surface area was measured by nitrogen adsorption at 77°K using 15 point BET.

B. Bulk Density (g/m^3)

For agricultural by-products and activated carbon from them bulk density was measured using the method of Ahmedna et al. (1997), which consisted of placing a known weight of activated carbon of 10-30 mesh size carbon in a 25 ml cylinder to a specified volume and tapping the cylinder for at least 1-2 min and measuring the volume of carbon. The bulk density was measured as:

$$\text{Bulk density (g/m3)} = \frac{\text{weight of dry sample (g)}}{\text{volume of packed dry sample (g)}}$$

C. Attrition/ Hardness (%)

The attrition of the samples was measured using wet attrition method described by Toles et al. (2000). 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 using Variomag Electronic Ruhrer Multipoint HP 15 stirrer (Daytona Beach, FL) with a 1/2 inch stir bar for agitation. The solution was then filtered through 50-mesh screen and the retained carbon was thoroughly washed and dried at 90°C under vacuum for 4 h and weighed. The % attrition was measured as:

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

a/ Adsorption of phenol and furfural from water solutions on sorbents.

D. Waste water treatment from organic impurities by activated carbon and agricultural by-products

Liquid chromatography is passed on HELCh / higher-effective liquid chromatography, detector Waters 486, controller Warers 600S, Pump, Waters 626, colon 250x4mm, Si-100 C 18, P 150 Bar, V 1ml/m, mobile phase acetonitryl-water (50:50), detector UV-254).

UV spectrometry is passed on UV-Specord spectrometr

Result and Discussion

Adsorption by agricultural by products is preferred because of its have low sensitivity to flow fluctuations and exhibits greater flexibility. The advantages of agricultural by-products in comparison with other sorbents are their low cost, availability of extraction, operational flexibility and control and others. 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 carbons.

The pore structures of breaking apricot and peach seeds, also activated carbon from them were determined as follows:

1. For mesopores the diameter range 50…2nm areas and volumes determined by N_2 adsorption technique at – 195^oC,
2. For micropores the diameter range less 2nm areas and volumes were determined by CO_2 adsorption measurements at 0^oC by the application of Dubinin-Radushkevich equation.
3. Here was not determined any measurement for macroporosity, because of it`s known that for activated carbon surface areas consists in generally with microporose (around 90%) and 6-10% only mesopores with small amount of macroporose.

Activated carbon is also used in water treatment plants for the removal of odors and tastes. Agricultural by products and activated carbons from them, on the other hand, can be made a renewable resource. Preliminary studies on cost estimation have shown that agricultural by-products can be manufactured for as $ 0,03 per 1kg and agricultural byproduct based activated carbons – $0,14 per 1 kg.

In the present study have describe the using of some fruits / apricot, peach / stones and based on them activated carbon. The technological scheme of use of such sorbents includes in itself set of difficulties. It have been solved a question with additional application of elastic bags with small holes impervious the filled sorbents.

Adsorption from wastewater with organic pollutants involves concentration of the solute on the surface. Here, it has been had adsorption and desorbtion process together which will attain an equilibrium state. Here is used the Dubinin-Radushkevich model for description of the adsorption data.

It`s known that activated carbon surface area has a nonpolar nature, but during the treatment process with some of chemicals, as acids for instance, this sorbents surface took slightly polar character, which is in future can be responsible for hydrophobic influence of this surface. In this case, as row stone materials and more activated carbon can be used for organic molecule sorbents [5]..

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 they 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.

The measurements for furfural in a water solution were carried out in concentration 0,01M. The furfural content in water before and after the sorption made a correction by liquid chromatography and UV spectrum also. The results are similarly, apricot stones based acid-activated carbon has higher sorptive 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 - Carbonsorb-AB.

From economical point of view the using of breaking stones can be effective. The using of stones also can be useful for future them treatment as burning agent in furnace.

Table 1.

Physical properties of experimental sorbents

Physical properties	Row peach stones breaking	Row apricot stones breaking	Peach stones based acid-activated carbon	Apricot stones based acid-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 Results (%)				
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

Table 2.

The sorption of phenol from water (0,05M)* solution on sorbents / Temperature 20°C, duration 4 hours /

N=	Sorbent	N_D^{20}after sorption	sorption g phenol./ g sorbent
1.	Row peach stones breaking	1.3321	0.0227
2.	Row apricot stones breaking / crushing/	1.3322	0.0219
3.	Peach stones based acid-activated carbon	1.3315	0.0289
4.	Apricot stones based acid-activated carbon	Full sorption	0.0395
5.	Carbonsorb-AB	Full sorption	0.0390

*N_D^{20} for initial phenol solution is1,3324

Table 3.

The adsorption of furfural 100 ml 0,01M furfural on agricultural by-products and activated carbon /1g/ / temperature 20°C, duration 4 hours /*

N=	Sorbent	The adsorption mg/g	The adsorption %
1.	Row peach stones breaking	0.12	12.8
2.	Row apricot stones breaking	0.14	15.0
3.	Peach stones based acid-activated carbon	0.29	25.0
4.	Apricot stones based acid-activated carbon	0.32	34.0

Technological decision during the flood

It`s known that during the flooding treatment and dispersal component is a trench system and it has inspection ports, the service provider may be able to pump water from the trenches to help the soil dry and aerate. However here it is necessary to take into account the following factors:

1 If the onsite wastewater treatment system has electrical components, an ability to restart the system will depend on the flood elevation.

2. If the flood water covered only the tanks and the components in the tanks, it`s possible to restart the system without further evaluation of the components.

3. If the flood water covered components located on the ground surface (air pumps, panels), the system should be inspected for determine whether it is safe to restart electrical service and use the system.

Alongside with this, a case of flooding naturally exists other difficulties for extraction sorption systems as usual cleaning river waters by cascade system. However, sorption materials can serve as a part of ground and can be removed after end of flooding.

With the purpose of the technological decision of a problem it is offered to create special space along coast of the river on achievement of former levels of a surface

of pollution to arrange dams with mobile walls filled by adsorbents.

The protective system for a river stream will consist of a primary treatment system and also secondary treatment where protective walls filled with proposed sorbents are established. Some walls with forward pools are desinged to create an opportunity for replacement of a sorbent.

Additionally, sorption materials can be placed on the floodplain, e.g., in ponds with mobile walls or elastic bags with small holes impervious filled by adsorbents, and removed after the flood. There would be a primary treatment system and a secondary treatment where the containers filled with activated carbon or agricultural by products from them are established.

Conclusion

It has been found advantageous to go on with the researches in organic pollutants

sorption by agricultural by-products and based on them activated carbons.

It has been offered the convenient method for successfully sorption phenols, furfural and probably other organic substances as BTEX / benzene, ethyl benzene, toluene and xylenes /, pesticides from water.

The treated natural materials can be propose for using as sorbents and as promising materials for waste water treatment from small enterprises.

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