

## TECHNOLOGICAL DESIGN OF FURFURAL ADSORPTION FROM WATER SOLUTIONS

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### INTRODUCTION

It has been investigated an adsorbitive abilities of zeolites as sorbents available in Armenia and Iran, in particular mordenite, clinoptilolite, and also H-mordenite, ZSM-5 in relation to organic pollutants for the purpose of device-technological design of process of waste water treatment. Here was studied as organic pollutant furfural.

Furfural is used as a solvent in petrochemical refining to extract dienes and aromatics from other hydrocarbones. 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 lubrication oils. Furfural is also an intermediate in the production of the solvents. The related compound hydroxymethylfurfural (which is derived from hexoses) has been identified in a wide variety of heat processed foods.

Furfural is an active monomer used for chemical compound synthesis. About 64% of furfural throughout production the world are used for furfuryl alcohol synthesis. Furfural, as well as its derivative furfuryl alcohol can be used either by themselves or together with others to make solid resins. 16% of furfural is directed for furan & tetrahydrofuran synthesis.

Furfural is a toxic substance – LD<sub>50</sub> 126mg/kg/, MPC in reservoirs - 1mg/l, in air - 0.05mg/m<sup>3</sup>. Furfural has an odor similar to almonds.

Furfural vapor is an irritant of the skin, eyes and respiratory tract. It may also cause unconsciousness. Long-term exposure to furfural may cause sensitization of the skin, loss of the sense of taste, numbness of the tongue, and breathing problems. Consequently the furfural existence in sewage and its removal is an actual problem.

Nowadays natural zeolites are focused in applications in the sector of wastewater decontamination, for instance for removal of ammonium from municipal sewage and abatement of radionuclides from effluents of nuclear power plants [1]. There are many reasons for zeolites using in mentioned fields: good selectivity for many

toxic cations and harmful compounds [1], as adsorbents for organic compounds [2,3].

### MATERIALS AND METHODS

Zeolites occur in nature in specific kinds of rocks. Zeolite rich rocks are widespread in Northern part of Armenia, occurring in very extended geological formations. The zeolite types are exclusively clinopilotite - in Idjevan / Northern-East of Armenia / and mordenite in Shirak / Northern-West of Armenia/. The one clinoptilolite sample used also in this study were obtained from Semnan province in Iran.

Taking advantage of their high zeolite content, high cation exchange capacity and selectivity many agricultural applications of zeolites have been proposed recently. Nowadays some of natural zeolites were characterized from the point of view of chemical composition, type of structure and chemical, thermal and radiation resistance.

Natural zeolites - mordenite and clinoptilolite were dehydrated at 400°C in vacuum (0.1 mm) for 3-4 hours. H-mordenite and ZSM-5 was prepared in our laboratory [2,3].

The removal of organic substances is carried out as follows.

The researches were spent in static conditions on a laboratory rocking chair. Sorbents brought in quantity of 1,0 ±0.01 g in water solutions, volume 100 ±0.1 ml containing furfural in quantity from the maximum solubility. Further a mix placed on a rocking chair and subjected to hashing during 6h., at temperature of 20°, then test definded within 24 h.

Furfural sorption. On 1 gr of sorbent added on 10ml solutions of furfural in water. The mix was carefully shaken up within 6 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.

Residual quantities of substances were defined by methods of UV-spectroscopy and HLECh (system Water 486-detector, Water 600S -

controller, Water 626-Pump, a column 250x4 mm filled microspherical silica as sorbent, speed of a stream of a mobile phase of 1 ml/mines).

On the basis of the analysis of data isotherms of adsorption which have been processed by means equations of Dubinin-Radushkevich, Langmuir, Freundlich have been constructed [4].

The elementary version of device-technological design of adsorbative waste water purifications is use of the block from two devices – the blender in which sorbent suspension in cleared water mixes up before achievement adsorbative balance, and sediment bowl in which fulfilled adsorbent separates from the cleared water. Calculation of such scheme, taking into account the maximum adsorption data of furfural from water environments the specified sorbents, has shown that the expense of the last is inadmissible is great (for example, in the case of furfural it will make 1,545 kg/l for H - mordenite, at initial concentration 1 g/l) [5,6]. Considerably to reduce the expense of adsorbent use of more perfect schemes of device design – crossing-step or counter-flow allows.

On the basis of the received experimental and settlement data mathematical models of the technological scheme of adsorbative water treating from noted pollutant - furfural have been deduced.

## RESULTS AND DISCUSSION

Adsorption of furfural by zeolites in isothermal conditions is preliminary studied at 20°C (293K ) and relation solid phase : liquid ( adsorbent : a furfural solution) = 1:100. Equilibrium concentration of furfural in a solution defined by UV - at  $\lambda = 260 \text{ nm}$ . Results of research are resulted in table 1 where equilibrium concentration are expressed in relative units  $C/C_s$ . Here  $C_s$  – concentration of the saturated solution of furfural at 20 °C, this concentration is equal  $C_s = 800 \text{ mmol/l}$  [1]. Adsorption isotherms in co-ordinates  $a = f(C/C_s)$  are presented at the picture 1.

An interpretation of isotherms made within the limits of the theory of volume filling of a micro pore ( TVFM ), according to [ 1 ] applicable and

**Table 1.** Adsorption of furfural from a water solution on zeolites at 293 To ( $C_s = 800 \text{ mmol/l}$ ).

$C/C_s$	Adsorption, $a$ , $\text{mmol/gr}_{\text{adsorbent}}$				
	Mordenite	H-	Clinoptilolite/ <sub>Arm</sub>	Clinoptilolite/ <sub>Iran</sub>	ZSM – 5
0,0044	0,058	0,125	0,070	0,076	0,170
0.0088	0,087	0,205	0,120	0,135	0,250
0,0170	0,126	0,261	0,270	0,295	0,353
0,0440	0,184	0,352	0,240	0,261	0,461
0.0610	0,210	0,404	0,260	0,278	0,510
0.0880	0,220	0,430	0,320	0,342	0,540
0,1320	0,256	0,465	0,350	0,375	0,590

to adsorption of the dissolved substances. Considering, that in most cases, volumes are distributed under the normal law, isotherms of adsorption of furfural on investigated adsorbents in co-ordinates of the equation of Dubinin-Radushkevich (equation DR).

$$\ln a = \ln a_s - (RT/E)^2 \cdot \{ \ln (C_s/C) \}^2, \quad (1)$$

where:  $C_s$  and  $C$  – concentration, accordingly, the saturated and equilibrium solutions;  $a$  and  $a_s$  - accordingly, equilibrium and maximum adsorptions.

The adsorption is maximum in the case of zeolite ZSM-5 ( table 1), that, apparently, it is possible to explain to that average diameter of its pore (0,75 nanometers) is more than Van-der-Waals diameter of a molecule of furfural (0,65 nanometers), from that furfural adsorption becomes possible not only on a surface of crystals of zeolite

(as in case of natural zeolites ), but also by partial introduction of molecules of furfural in a mouth of pore. It should be note that clinoptilolite from Semnan more actively to its Armenian analogue.

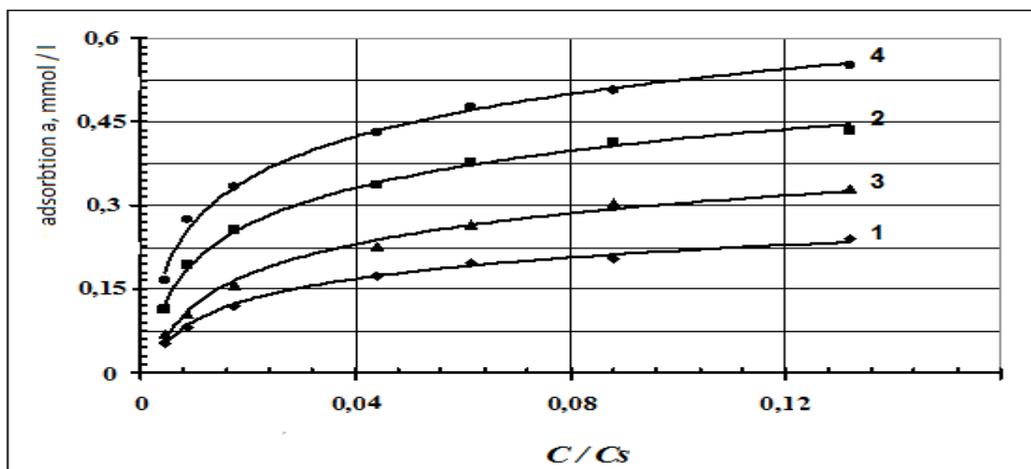
While transfer of mordenite in the H-form, apparently, took place partial dealuminated zeolite, with destruction of a part of tetrahedrons  $(Al_4O)^{-3}$  and, as consequence, expansion of some part of pore, as has led to quantity increase of sorpted furfural, in comparison with initial mordenite. Values of characteristic energy of furfural adsorption on the investigated sorbents are close between themselves and, with confidential probability 0,86, it is possible to accept  $E = 9,5 \pm 1,2 \text{ Kgooule/mol.}$

On superficial groups of hydro group and atoms of oxygen of H-zeolites processes of formation of chemical bonds owing to molecular

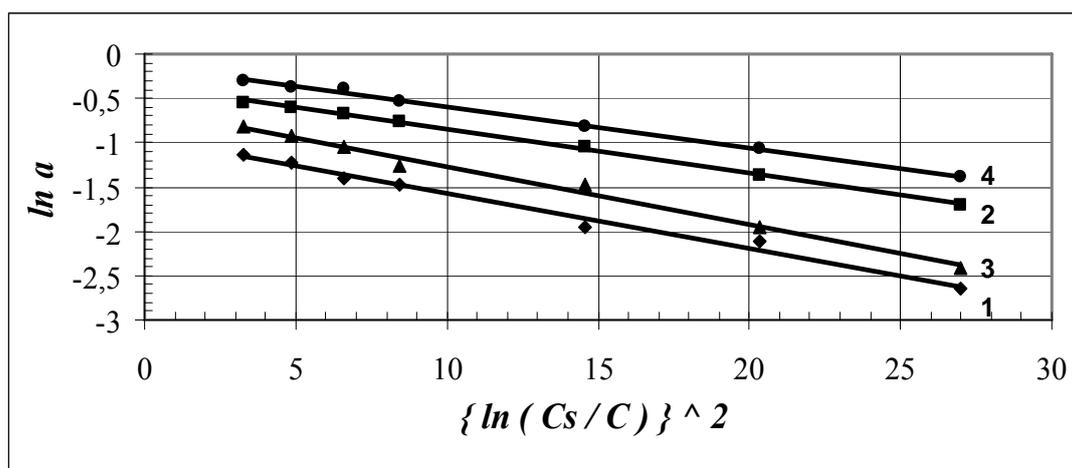
interactions with group of carboxyl in furfural proceed.

Kinetic researches of adsorption spent in a cylindrical reactor in diameter 72 mm supplied

propeller type mixer in diameter of 18 mm. A mixer drive – noncontrollable,  $n = 600 \text{ min}^{-1}$  ( $10 \text{ sek}^{-1}$ ).



**Figure 1.** The isotherms of furfural sorption from water solutions on zeolites  
1- natural mordenite, 2-natural clinoptilolite/Iran, 3. natural clinoptilolite/Arm 4 ZSM-5



**Figure 2.** Isotherms of furfural adsorption on zeolites  
in Dubinin-Radushkevich equation coordinates  $\ln a = f \{ \ln (C_s / C) \}^2$

Suitability of a mixer for creation of suspension with uniform of adsorbent distribution in liquid volume was checked on condition  $Re_m \geq Re_m^*$ , where  $Re_m^*$  - boundary value of criterion of Reynolds for a mixer, providing creation of uniform suspension,  $Re_m$  - value of the same criterion for a used mixer. Value  $Re_m^*$  is equal [4]:

$$Re_m^* = C \cdot Ar \cdot (d_s / d)^{0,5} \cdot (D/d)^k \quad (2)$$

There are:

$Ar = d_s^3 \cdot (\rho_{m6} - \rho_{\text{жс}}) \cdot \rho_{\text{жс}} \cdot g / \mu^2$  - Archimed criterion for solid phase,

$C$  и  $k$  - constant for propeller mixer,

$C = 6,6$ ,  $k = 1$ ;  $d_s$  - equivalent diameter of particles ( $d_s = 0,375 \text{ mm}$ ),

$d = 18 \text{ mm}$  - mixer diameter,

$D$  - diameter of reactor,

$\rho_{\text{sol}} = 2160 \text{ kg/m}^3$  - zeolite density,

$\rho_{\text{liquid}}$  and  $\mu$  - density and viscosity of liquid phase, at  $20^\circ\text{C}$ ,

$\rho_{\text{liquid}} = 997 \text{ kg/m}^3$ ,  $\mu = 0,894 \cdot 10^{-3} \text{ pa}\cdot\text{sec}$ ,  $g = 9.81 \text{ m/sec}^2$ .

In table 2 the parameters of equations DR received by processing MLS (a method of the least squares) the isotherms resulted on rice are resulted. 2. The correlation factors are calculated for received regressive equations, are rather close to unit that

testifies to applicability TVFM to adsorption process of furfural on the investigated zeolites.

**Table 2.** The parameters of Dubinin-Radushkevich equation during the furfural adsorption on zeolites.

№ zeolites	The equation of regression	$R^2$	$a_s$ , mmol/gr	$E$ , kJ/mol
1	$\ln a = -0,9242 - 0,0638 \{ \ln (C_s/C) \}^2$	0,9981	0,389	9,81
2	$\ln a = -0,3638 - 0,0494 \{ \ln (C_s/C) \}^2$	0,9997	0,695	11,1
3	$\ln a = -0,6031 - 0,0668 \{ \ln (C_s/C) \}^2$	0,9988	0,547	9,58
4	$\ln a = -0,1362 - 0,0460 \{ \ln (C_s/C) \}^2$	0,9992	0,872	11,5

After substitution of numerical values, we receive  $Re_m^* = 2856$ . The used mixer provides value of criterion of Reynolds:

For reduction of an error of the experiment arising at sampling because of possible infringement of set relation solid :liquid and equilibrium concentration of furfural, volume of a reactionary mix, in comparison with experiments at research adsorptive balance till 500 ml have been increased. At such initial volume of a mix, selection 8 ÷ 10 tests at 1 ml practically does not affect a process course.

The kinetic curve of furfural adsorption is resulted on figure 3 at  $C = 20$  mmol /l in coordinates  $\gamma = f(\tau)$ , there is:

$\gamma$  – relative approach of adsorption to balance;  $\gamma = a_\tau / a$ . Here are

$a_\tau$  – current value of adsorption at the moment of time,

$\tau, a$  – an equilibrium value of furfural adsorption in solution 18 mmol /l.

The speed of approach to balance in the conditions of experiment, practically not depend from a kind of adsorbent; in all cases balance was reached for 180 ÷ 190 min. The dependence of  $\gamma = f(\tau)$  It is almost linear on an extent ~ 80 % of all time of an establishment of balance (till contact 120 ÷ 150 мин). Such behavior of process is characteristic for cases when speed of adsorption is supervised external diffusion mass transfer [5] that is possible as in case of rather fast, in comparison with external, internal mass transfer, and in case of its absence.

If for natural clinoptilolite and mordenite internal diffusion (and, hence, internal mass transfer) cannot have places because of small diameter of a time ZSM--5, (and, probably, some part of time H-mordenit) have diameter, a little больший, than Van-der-Waals diameter of a molecule of furfural (0,75 nanometers, at diameter of a molecule of furfural of 0,65 nanometers). An absence of the appreciable contribution internal

pore (up to adsorption of ~90 % from equilibrium) in kinetic of furfural adsorption in this case follows diffusion, apparently, attribute to increase in effective diameter of adsorbate molecule because of hydration that limits adsorption only to area a mouth of pore a time and so complicates diffusion of hydrate molecules in pore space, that the share diffusions in mass transfer becomes sighting small. Apparently, basically, for this reason adsorption of furfural also has smaller size, than the porous structure of zeolite allows. In favor of this assumption says that fact, that adsorption of furfural from tetrachloromethan (no hydrated solvent) zeolite ZSM--5 has size 0,31  $\mu$  [6], or 3.3 mmol/g, that almost in 4 times exceeds size of its maximum adsorption from water ( $a_s = 0,872$  mmol/g).

From specific equation ( $a = (C_0 - C) \cdot V / g$ ) follows, that the expense of adsorbent for cleared water volume ( $m$ ) can be according:

$$m = (C_0 - C_k) / a_k \quad (3)$$

Here  $C_0$  and  $C_k$  - accordingly, initial and final concentration of furfural,  $a_k$  - size of adsorption, equilibrium with  $C_k$ . As a rule,  $C_k$  has rather small size; even at use of the cleared water only in system of the closed water turn,  $C_k$  usually does not exceed ~ 0,1 mmol/l.

If to consider, that so low concentration are answered with low sizes of equilibrium adsorption, it is easy to see, that the expense of adsorbent, at such registration of process, is inadmissible is great. From equation (3), taking into account (1), to a kind:

$$m = (C_0 - C_k) / a_k = (C_0 - C_k) / \exp \{ \ln a_s - (RT/E)^2 \cdot [ \ln (C_s/C_k) ]^2 \} \quad (4)$$

And substituting corresponding values in (4) it is received, that at decrease in concentration of furfural for the closed system of a water turn (0,1 mmol/l), the specific expense of a sorbent ( $m$ ) will water, a step ( $k$ ) where, contacting to partially

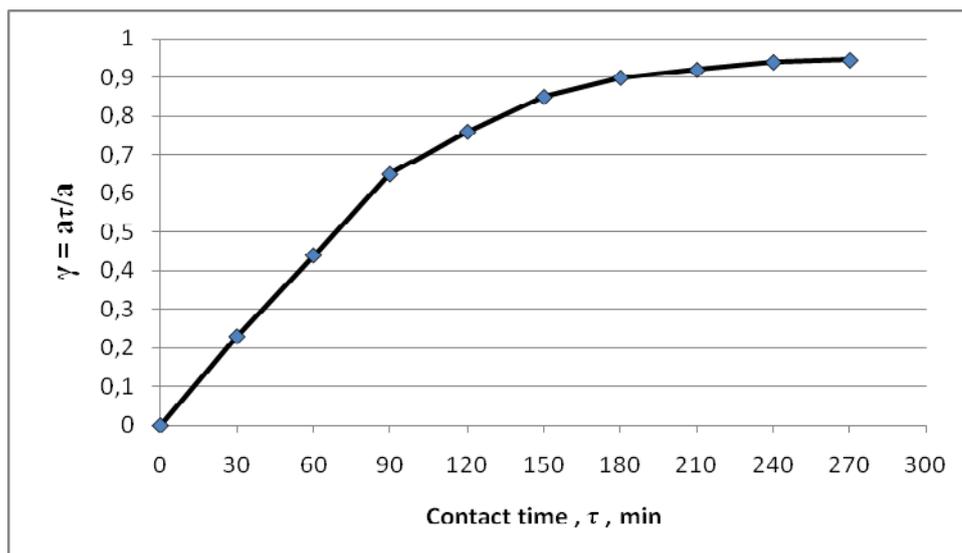


Figure 3. Kinetic curve of furfural adsorption.

make 1,745 kg/l for *H* - mordenite, and for zeolite *ZSM-5* – 1.04 kg/l.

As technological design are offered cross-step or counter-flow schemes for waste water treatment process. At equal number of the basic devices in the considered schemes preference it is given counter - step scheme. As in both considered schemes at equal number of the basic devices and, hence, identical capital investments when

economic feasibility is defined by operational expenses, preference, certainly, it is necessary to give counter flow-step scheme.

It is most full used of adsorptive capacity of sorbent at counter-flow mutual moving of adsorbent and treated water (figure 4). Here is presented the counter flow-step scheme.

An adsorbent is brought in the amalgamator-sediment bowl of last, on a course of

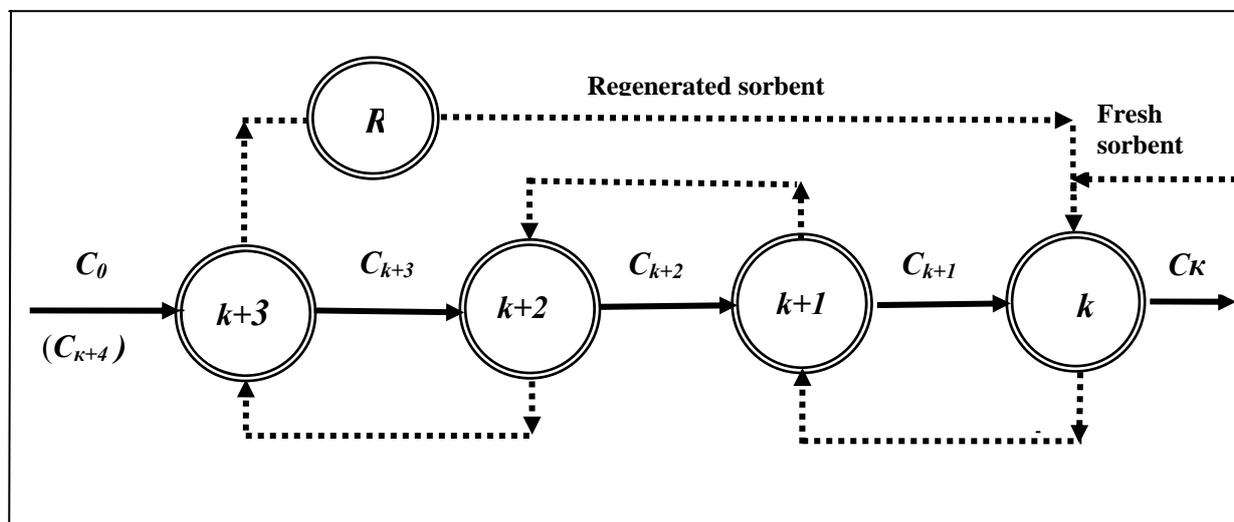


Figure 4. The counter-flow scheme for adsorptive water purifications *k, k+1, k+2, k+3* – units "amalgamator-sediment bowl"; *R*- regeneration knot of adsorbent.

cleared water (concentration of furfural  $C_{k+1}$ ), adsorbs furfural before achievement to specific adsorption ( $a_k$ ), equilibrium with the set final concentration ( $C_k$ ) it in water. After upholding, water, cleared to  $C_k$ , leaves installation, and adsorbent, using only small part of the adsorptive capacities, is transferred to a step  $k+1$  where

adsorbs furfural before achievement of adsorption, equilibrium with  $C_{k+1}$ .

The defended water, with concentration of furfural  $C_{k+1}$ , arrives on a step  $k$ , and adsorbent – on a step  $k+2$ . As a result of repetition of the described operations, adsorbent is deduced with last, on a sorbent course (and the first – on a water course), steps, having reached size of specific adsorption, a

little smaller, than equilibrium with initial concentration of furfural in water  $C_0$ . The mathematical description of process is realized by a step-by-step method.

## CONCLUSION

The elementary version of device-technological design of water treatment from furfural is proposed the block from two devices – the blender in which sorbent suspension in treated water mixes up before achievement adsorptive balance, and sediment bowl in which fulfilled adsorbent separates from the cleared water. For reduce the expense of adsorbent use of more perfect schemes of device design – crossing-step or counter-flow allows.

As both considered schemes contain equal number of the basic devices and, hence, are practically identical on demanded capital investments and operational expenses, the preference have been gives to counter-flow step scheme.

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